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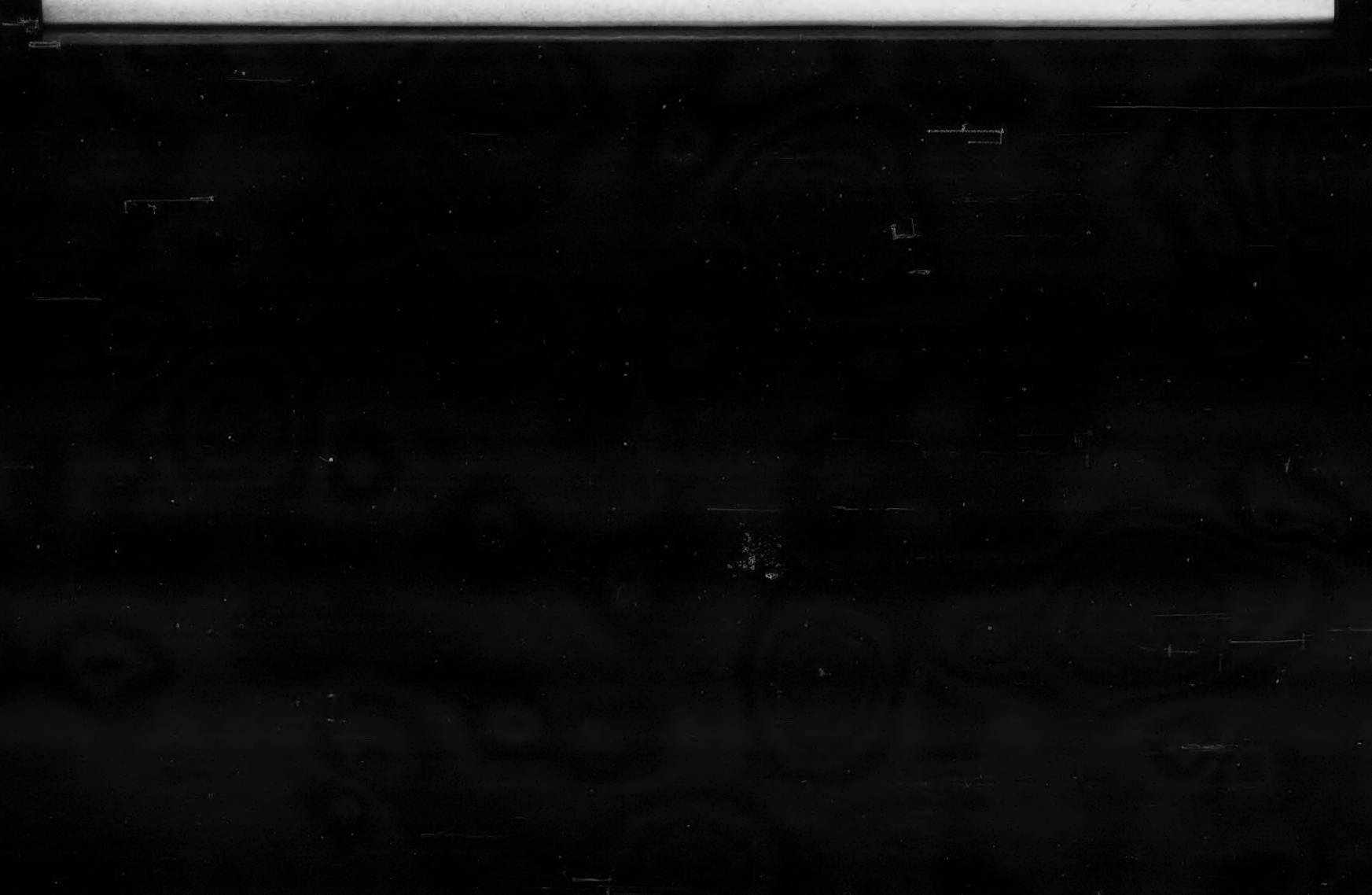

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VOL. 29 JANUARY, 1951 NUMBER 1

VAPOR-PHASE PRODUCTION OF DIMETHYLANILINE[1]

BY T. H. EVANS AND A. N. BOURNS[2]

Abstract

Formation of dimethylaniline by vapor-phase reaction of (*a*) aniline and methanol and (*b*) aniline and dimethyl ether has been investigated. Activated alumina was the most efficient catalyst. Reaction (*b*) was preferred since higher yields of purer product were obtained at lower temperatures. Aniline reacted with five moles dimethyl ether over Alcoa. Activated Alumina at 275° to 285°C. gave a quantitative yield of dimethylaniline of 99% purity. A small pilot plant was constructed and operated continuously for the production of 4 to 5 lb. dimethylaniline per hr.

Introduction

This problem was undertaken in the later stages of the war owing to interest shown in the antiknock effectiveness of aromatic amines in aviation fuels. Dimethylaniline may be manufactured by autoclave reaction (10) of aniline and methanol in the presence of an acid catalyst. A yield of 95% based on aniline is obtained; the net yield based on methanol is somewhat lower. The product contains not more than 0.4% monomethylaniline. The disadvantages of the process are: (*a*) an autoclave is required for this batch process; (*b*) a caustic soda treatment is necessary before distillation of the product; (*c*) a considerable loss of methanol results from the formation of dimethyl ether which escapes during the blowoff at the end of the run.

The object of this investigation was the development of a process whereby dimethylaniline could be produced continuously by the vapor-phase reaction of methanol and aniline over solid dehydration catalysts. Although this reaction was first reported about thirty years ago (8), no good laboratory process has been published, and the recent patent literature (9) is the best source of information.

Activated alumina has proved to be the most suitable catalyst for this reaction.

$$C_6H_5NH_2 + 2CH_3OH \longrightarrow C_6H_5N(CH_3)_2 + 2H_2O$$

[1] *Manuscript received August 17, 1950.*
Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

[2] *Present address, McMaster University, Hamilton, Ont.*

Other dehydration catalysts were unsatisfactory either because considerable quantities of monomethylaniline resulted from incomplete reaction, or nuclear (C–) methylated products resulted from rearrangement of the normal N-methylated products.

When optimum conditions of temperature, contact time, and ratio of methanol to aniline were employed, the resulting product contained 96% dimethylaniline, with the remainder mainly monomethylaniline. Methanol was used in excess and a considerable quantity of this excess was converted to dimethyl ether. In any industrial process, it would be necessary to use this dimethyl ether for the methylation of aniline to dimethylaniline.

Attention was then turned to the reaction of dimethyl ether and aniline over activated alumina. Practically all the worthwhile published information on this reaction also is found in the patent literature (3, 7) and B.I.O.S. reports (5). The latter brief description of the I. G. Farbenindustrie process at Ludwigshafen (5) became available after the experimental work of this paper was completed. The similarity between these two independently developed processes is very marked; our process required proportionately less dimethyl ether than the German process.

It was found that the product of this reaction contained more than 99% dimethylaniline, even under milder conditions of temperature and contact time than required for the methanol–aniline reaction. Thus the problem eventually resolved itself into two parts:

1. The production of dimethylaniline by the catalytic vapor-phase dehydration of dimethyl ether and aniline.

$$C_6H_5NH_2 + (CH_3)_2O \longrightarrow C_6H_5N(CH_3)_2 + H_2O$$

2. The production of dimethyl ether by the catalytic vapor-phase dehydration of methanol.

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

This reaction will be the subject of a later paper.

Preparation of Dimethylaniline

Sources of Reactants and Catalysts

Reactants were used without purification and were obtained from the following sources:

(*a*) Aniline from Naugatuck Chemicals, Elmira, Ont.

(*b*) Methanol (Synthetic, C.P.) from Standard Chemical Co., Toronto.

(*c*) Dimethyl ether (minimum purity 99.5%, usually in cylinders containing 50 lb.) from DuPont & Co., Belle, W.Va., or Ohio Chemical Co., Cleveland.

Small samples of catalysts (Tables I, III) were obtained from the various sources listed. Harshaw Activated Alumina (pellets, $\frac{1}{8}$ or $\frac{1}{4}$ in.) was purchased from the Harshaw Chemical Co., Cleveland, and Alcoa Activated Alumina (Grade F–1, 4 to 8 mesh) from Prescott & Co., Montreal.

Isolation and Analysis of Products

The product obtained using either methanol or dimethyl ether consisted of two layers. One layer contained the methyl anilines, methanol, dissolved ether, and a small quantity of water while the second layer consisted mainly of water and methanol with a small quantity of dissolved ether and aniline derivatives. The relative density of the layers was determined by the amount of methanol present.

Separation of the two layers was facilitated by the addition of sodium chloride. The aqueous layer was extracted with a small quantity of ethyl ether and the combined organic layers dried over sodium hydroxide. The product was obtained by distillation under reduced pressure (10 to 15 mm.). If the dimethylaniline content was greater than 85%, analysis for tertiary amine content only was made, otherwise analyses for primary, secondary, and tertiary amine contents were carried out.

Aniline was determined by the picryl chloride method (6).

Aniline plus monomethylaniline was determined by acetylation with acetic anhydride, followed by hydrolysis of excess anhydride and titration of the acetic acid formed with standard sodium hydroxide solution.

Tertiary amines (dimethylaniline and nuclear-methylated dimethylaniline) were determined by the method of Haslam and Hearn (4). Primary and secondary amines were acetylated with acetic anhydride, the acetylation products dissolved in glacial acetic acid, and the dimethylaniline titrated with a standard solution of perchloric acid in glacial acetic, α-naphthol benzein being used as indicator.

Refractive index measurement served as an indication of the extent of ***ring methylation***. The refractive indices of the various methylated anilines are as follows:

Compound	η_D^{20}
Aniline	1.5863
Monomethylaniline	1.5714
Dimethylaniline	1.5588
p-Methyldimethylaniline	1.5366
o-Methyldimethylaniline	1.5153

The refractive index of dimethylaniline containing less than 2% monomethylaniline is the same as that of pure dimethylaniline, η_D^{20} 1.5588. The presence of any ring methylated material is indicated by a lower refractive index. Since dimethyl ether usually yields dimethylaniline containing less than 3% monomethylaniline, the presence of ring methylation is readily detected in this manner.

The Reaction of Aniline and Methanol

Influence of Catalyst

Preliminary experiments indicated the catalyst most suitable for the formation of dimethylaniline from aniline and methanol. The catalyst tube consisted of a 20 mm. O.D. Pyrex tube 22 in. long packed with catalyst (usually 4 to 8 mesh) for a length of 16 in. The tube was electrically heated from without and the temperature was measured by means of a mercury thermometer embedded in the catalyst. The methanol–aniline mixture was fed directly into the catalyst tube from a burette. Table I gives the catalysts

TABLE I

CATALYSTS FOR VAPOR-PHASE PRODUCTION OF DIMETHYLANILINE FROM ANILINE AND METHANOL

Catalyst	Yield of tertiary amine, %	Extent of rearrangement*
Silica Gel (Davco)	50	
Silica Gel (Infilco Hypersil)	15	
Activated Al_2O_3 (Harshaw)	85	+
Al_2O_3–Fe_2O_3 (20%) (Harshaw)	50	
Al_2O_3–TiO_2 (Harshaw)	75	Trace
Al_2O_3–Cr_2O_3 (Harshaw)	30	
Filtrol (activated silicate)	50	+++
Bentonite (activated silicate)	80	+++
Magnesia (Harshaw)	0	
Bone + phosphoric acid	75	
U.O.P. polymerization catalyst	90	++++

* *Extent of rearrangement—slight*, +.
considerable, ++.
very great, ++++.

used and results obtained under most favorable conditions (usually 350° to 375° C., 10 cc. per hour of a solution of five moles methanol and one mole aniline).

Activated Alumina (Harshaw) was the most efficient catalyst, since it gave a high yield of dimethylaniline and a small amount of rearrangement products. Later it was found that Alcoa Activated Alumina Grade F–1 was an even more efficient catalyst for this reaction.

Activated Alumina Catalyst

In order to determine the optimum conditions of temperature, contact time, and methanol–aniline ratios for the formation of dimethylaniline, a larger laboratory apparatus was employed. This apparatus consisted of two zones, preheater and catalyst, each with separate heat control (rheostats). Heat was supplied by a helical coil of chromel A resistance wire wound about the spiral grooves of an alundum core refractory surrounding the zone. The preheater was a Pyrex tube 32 mm. O.D. about 24 in. long packed with limestone chips for heat transfer. It was connected by means of a ground joint to a Pyrex

catalyst tube, also 32 mm. O.D. about 30 in. in length packed with 300 cc. of catalyst (4 to 8 mesh). Temperatures in preheater and catalyst were measured by means of thermocouples, movable along wells concentric with the tubes.

Aniline and methanol mixed in the desired ratio were introduced into the preheater where they were vaporized and preheated to the required temperature before entering the catalyst zone. A prerun was always made before collection of the product, in order to establish equilibrium conditions of adsorption of reactants and products on the catalyst. The reaction products were condensed by means of a Friedrich condenser and isolated as previously described.

After each run, the catalyst was regenerated by passing air over it for two to three hours at a temperature of 500°C. for Harshaw Alumina and 425°C. for Alcoa Alumina. This served to remove adsorbed reactants and products. The presence of carbonaceous material on the catalyst was not detected under any of the conditions studied. Although no apparent loss in activity was detected, the catalyst was discarded after three to five regenerations, in order to ensure comparable activity in all experiments.

Table II summarizes the results obtained using Harshaw Alumina and Alcoa Grade F–1 Alumina as catalysts for the methanol–aniline reaction. Alcoa F–1 Alumina gives a higher conversion at a lower temperature than Harshaw Alumina. The highest yield of dimethylaniline using the Harshaw catalyst was 95% at 325°C. with a molar ratio methanol to aniline of 10: 1. Some rearrangement products were present as indicated by the refractive index.

The optimum conditions using Alcoa Alumina, 285°C. and a molar ratio of 10: 1, produced a 95.5% yield of dimethylaniline. The refractive index of the product was the same as that of pure dimethylaniline. This indicated some rearrangement products since the monomethylaniline content of 4.5% would raise the refractive index, in the absence of nuclear methylation, above that of pure dimethylaniline. With both catalysts, milder conditions than optimum gave a lower yield of dimethylaniline while more drastic conditions of temperature and contact time gave increased rearrangement. Space velocities for high conversion are extremely low. The space velocities of 0.10 to 0.20 for total reactants are equivalent to only 1 to 2 cc. aniline per 100 cc. of catalyst per hour.

Reaction of Aniline and Dimethyl Ether on Laboratory Scale

The same apparatus was used for laboratory experiments with dimethyl ether as with methanol. Ether was passed at a constant rate from a cylinder through a flowmeter. The following catalysts were used:

(*a*) Harshaw Activated Alumina.
(*b*) Alcoa Activated Alumina, Grade F–1.

TABLE II

PRODUCTION OF DIMETHYLANILINE FROM ANILINE AND METHANOL

Run No.	Space velocity*		Temp., °C.	Dimethyl-aniline, %	η_D^{20}	Rearrangement**
	Aniline	Methanol				
Harshaw Activated Alumina (300 cc.)						
Al XX	0.017	0.085	300	70	1.5632	
" V	0.20	1.0	350	26	1.5714	
" IV	0.14	0.68	350	53	1.5658	
" II	0.07	0.34	350	75	1.5620	
" VIII	0.03	0.16	350	85	1.5600	
" IX	0.017	0.085	350	92.5	1.5588	+
" XXI	0.01	0.10	300	79	1.5610	
" XXII	0.01	0.10	325	95	1.5588	Trace
" XI	0.04	0.40	350	83	1.5605	
" X	0.02	0.20	350	92.5	1.5591	Trace
" XII	0.01	0.10	350	94	1.5587	+
Alcoa Activated Alumina Grade F-1 (300 cc.)						
Alcoa 8	0.016	0.16	275	84.5	1.5605	
" 11	0.01	0.10	285	95.5	1.5588	Trace
" 9	0.014	0.14	300	96	1.5584	+
" 10	0.01	0.11	300	95.5	1.5579	++
" 12	0.02	0.20	305	93.5	1.5588	+
				Pure	1.5588	

* *Moles of reactant per 100 cc. of catalyst per hr.*
** *Extent of rearrangement—slight,* +.
considerable, ++.
very great, ++++.

(*c*) Porocel, an activated bauxite manufactured by Attapulgus Clay Co., Philadelphia, Pa.

(*d*) Unigel, a Harshaw alumina gel.

Black iron pipe (1 in.) was substituted for Pyrex tubing in preheater and reactor in certain experiments in order to determine the effect of iron on the reaction.

Since the activities of fresh samples of catalysts were found to be variable, only the results of experiments using regenerated catalysts were considered significant. The fresh catalyst may contain some boehmite which is dehydrated during regeneration to γ-alumina (2), the catalytically active form, whereas the regenerated catalyst presumably is composed entirely of γ-alumina. Very little decrease in catalyst activity was noted after successive regenerations. However, catalysts were discarded after three to five regenerations, to ensure that results would be on a comparable basis.

The reactions of aniline both with methanol and with dimethyl ether are exothermic, and considerable temperature elevation occurs where the reactants first meet the catalyst. With a larger apparatus (see below), some provision must be made for the dissipation of this heat of reaction.

The results of the dimethyl ether experiments are given in Table III. As in the case of the methanol–aniline experiments (Table II), Alcoa F–1 Alumina catalyst was superior to Harshaw Alumina for the production of dimethyl-

TABLE III

PRODUCTION OF DIMETHYLANILINE FROM ANILINE AND DIMETHYL ETHER

Run No. and catalyst	Space velocity†		Temp., °C.	Dimethyl-aniline, %	n_D^{20}	Rearrangement††
	Aniline	Dimethyl ether				
Harshaw Alumina (300 cc.)						
12	0.018	0.18	250	75.5	1.5615	
14	0.018	0.18	275	96.5	1.5589	−
10	0.018	0.18	300	98.5	1.5586	+
22*	0.02	0.20	300	98	1.5588	−
7	0.037	0.37	300	92.5	1.5593	−
8	0.018	0.09	300	98	1.5587	Trace
3	0.037	0.18	300	95	1.5591	
1	0.073	0.37	350	97	1.5584	+
Alcoa F–1 Alumina (300 cc.)						
Al 3	0.018	0.09	225	92	1.5592	
Al 5	0.018	0.09	250	99	1.5588	−
Al 6	0.037	0.18	275	99	1.5588	−
Al 7	0.055	0.27	275	98	1.5588	−
Al 8	0.073	0.37	285	98.5	1.5588	−
Al 1	0.018	0.09	300	98	1.5583	+
Al 4*	0.08	0.40	285	98	1.5588	−
Al 5*	0.08	0.40	300	98.5	1.5588	−
Al 6*	0.08	0.24	300	97.5	1.5588	−
Porocel (300 cc.)						
PO I	0.037	0.22	305	....	1.5468	++++
III	0.037	0.22	275	93.5†††	1.5549	+++
II	0.045	0.23	255	95	1.5579	++
IV	0.037	0.22	235	95	1.5588	−
V	0.037	0.22	235	96	1.5585	+
VI	0.037	0.20	225	....	1.5615	−
Unigel (300 cc.)						
1	0.045	0.27	275	98	1.5584	+
2	0.045	0.25	255	98	1.5588	−
3	0.045	0.25	245	97.5	1.5588	−
6	0.073	0.40	255	95.5	1.5591	−
				Pure dimethyl-aniline	1.5588	

* *Iron reactor.*

† *Moles reactant per 100 cc. catalyst per hr.*

†† *Extent of rearrangement—slight, +.*
considerable, ++.
very great, ++++.

††† *% Tertiary amine determined as dimethylaniline.*

aniline. With the Alcoa catalyst, dimethylaniline of higher purity could be obtained at lower temperatures and shorter contact times. The tendency toward nuclear methylation was greatly reduced under these milder reaction conditions.

Porocel yielded large amounts of rearrangement products from aniline and dimethyl ether at 300°C. and even at 275°C.; it was quite active at temperatures as low as 235°C. However, the occurrence of some nuclear methylation even at 235°C. limited the study of this catalyst to this laboratory size apparatus.

Unigel was quite active at temperatures as low as 250°C. However, investigation was confined to the laboratory size apparatus since Unigel was not available in commercial quantities.

Dimethylaniline of 98.5 to 99% purity was obtained with Alcoa Alumina at 275° to 300°C. using a dimethyl ether–aniline ratio of 5: 1 and at rates as high as 8 cc. aniline per 100 cc. catalyst per hour. Under these conditions, no significant amounts of rearrangement products were obtained.

Life of Catalyst and Regeneration

In order to determine the life of the catalyst, a run of seven days' duration was made with Alcoa Alumina under carefully controlled conditions: temperature 295° to 300°C., rate 20 cc. aniline per hour (space velocity 0.073), catalyst 300 cc., and molar ratio dimethyl ether to aniline 5: 1. Previously aniline and dimethyl ether had been passed over the catalyst at 300°C. for one hour followed by regeneration.

During the course of this seven day run, the per cent dimethylaniline in the product decreased more or less uniformly from 98 to 96%, i.e. approximately 0.3% per 24 hr. Regeneration (see above) at the end of the seven day period followed by a short run under identical conditions gave a product containing 97% dimethylaniline. The activity of the catalyst was thus not restored to its original value.

Various methods of regeneration were attempted, e.g. the use of steam (2) and air and mixtures of the same at different temperatures, but catalyst activity, as indicated by the dimethylaniline content of the product, was not increased. This would indicate either a permanent poisoning of the catalyst or some change in its physical structure resulting in a loss of surface area.

Production of Dimethylaniline by a Two-Step Process

Since it was desirable to obtain dimethylaniline of better than 99.5% purity in order to eliminate the necessity of chemical purification, the possibility of conducting the reaction in two stages was next considered. If the material from the first stage (about 90% dimethylaniline) freed of water, was again passed over the catalyst, together with dimethyl ether, the resulting product should be approximately 100% dimethylaniline.

Table IV gives the results of the second step in the two-step process with Alcoa F-1 Alumina. In Run 28, the material used was 96% dimethylaniline obtained during the latter part of the seven day continuous run (above). The catalyst for Run 28 was that resulting from the seven day run, treated by passing air over at 425°C. for three hours.

TABLE IV

TWO-STEP PROCESS FOR PRODUCTION OF DIMETHYLANILINE USING DIMETHYL ETHER. SECOND STEP

Run No.	% Monomethylaniline in feed	Space velocity*		Temp., °C.	% Dimethylaniline in product	η_D^{20}	Re-** arrangement
		Methyl ether	Methylated anilines				
Alcoa 22	4†	0.05	0.05	280	99.5	1.5586	+
23	5†	0.06	0.10	280	99.5	1.5587	Trace
24	5†	0.06	0.10	250	99.5	1.5587	Trace
25	5††	0.06	0.10	250	99.5	1.5588	—
26	10††	0.13	0.11	250	99.5	1.5588	—
28	4†	0.05	0.10	250	99.5	1.5587	Trace

* *Moles reactant per 100 cc. catalyst per hr.*
** *Extent of rearrangement—slight, +.*
considerable, ++.
very great, ++++.
† *Resulting from one passage over Alcoa Alumina, Table III.*
†† *Synthetic mixture, prepared from pure dimethylaniline and monomethylaniline.*

The two-stage process thus yields an excellent product almost entirely free from monomethylaniline or rearrangement products. Run 28 indicates that a catalyst already used for seven days in the first stage of the process will still produce dimethylaniline of almost 100% purity when used in the second stage even at reduced temperatures and shorter contact times. The product from the first stage need not be dried nor distilled, as long as the water layer is removed.

PILOT PLANT PRODUCTION OF DIMETHYLANILINE USING DIMETHYL ETHER

A small pilot plant with a capacity of 4 to 5 lb. of aniline per hour was constructed. This figure was based on the assumption that space velocities found optimum in the laboratory experiments would be applicable on the pilot plant scale. This apparatus is shown in Fig. 1; letters in the text refer to this figure.

The plant consisted of an aniline feed system, dimethyl ether feed system, vaporizer (V), preheater (P), reactor (R) containing activated alumina catalyst, heat exchange system (H, H_1) (oil circulation), liquid condensing system (C_1, C_2), and dimethyl ether recycling system (E).

Aniline and dimethyl ether were vaporized in the vaporizer (V) and their temperatures regulated in the preheater (P) prior to reaction over the catalyst.

The liquid products, dimethylaniline and water, together with by-products such as methanol, were condensed, and the excess dimethyl ether was circulated from the receiver (L) back into the vaporizer (V). Hot oil was continuously circulated in a pipe (H_1) through the reactor (R) in order to maintain reasonably uniform temperatures throughout the reactor.

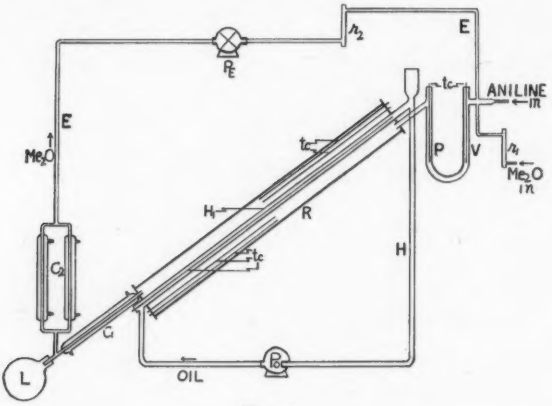


FIG. 1.

General Description of Apparatus

Aniline Feed System

Aniline was pumped at a constant rate from a 10 gal. drum by means of a Wilson Pulsafeeder, Type DES–1.* The aniline feed line was $\frac{1}{4}$ in. black iron pipe, with inserts of Pyrex at intervals for visibility and convenience (drainage stopcocks, etc.). Neoprene is admirably suited for these glass to iron connections and will withstand cold aniline for more than a year.

Dimethyl Ether Feed System

Dimethyl ether was supplied from a cylinder (containing 50 lb.) and the rate of flow controlled by a Hoke needle valve and measured by a Schutte and Koerting rotameter (r_1) size number 2–$\frac{1}{2}$ in. The dimethyl ether feed line was $\frac{1}{4}$ in. black iron pipe.

Vaporizer (V)

The vaporizer (V) consisted of a $1\frac{1}{2}$ in. black iron pipe 22 in. long packed with fine steel turnings and heated electrically. The thermocouple well was a $\frac{1}{8}$ in. black iron pipe, about 19 in. long, closed at one end, and concentric with the vaporizer. Aniline and dimethyl ether feed lines entered near the top of the vaporizer, which was in a vertical position 6 to 8 ft. above the floor. The bottom of the vaporizer was attached to the bottom of the preheater (P) by means of a U-tube (radius about 4 in.) of 1 in. black iron pipe.

* *Manufactured by Wilson Chemical Feeders Inc., Buffalo, N.Y., now distributed by Lapp Process Equipment Division, Lapp Insulator Co. Inc., LeRoy, N.Y.*

Preheater (P)

The preheater (P) was an 18 in. length of 1 in. black iron pipe, packed with marble chips (4 to 8 mesh), and heated electrically. The thermocouple well was a $\frac{1}{8}$ in. black iron pipe, about 17 in. long, closed at one end, and concentric with the preheater. The latter, suspended vertically, was attached at the bottom (see description of vaporizer (V)) by means of the U-tube to the vaporizer. The preheater outlet, which led to the reactor (R), was a 7 in. length of 1 in. black iron pipe welded at a 45° downward slope to the preheater about 3 in. below the top.

Reactor (R)

The reactor (R) was a 6 in. black iron pipe, 6 ft. long, with machined plain straight face flanges at each end. Machined black iron end plates ($\frac{1}{2}$ in. thick) were bolted to the flanges, and leaks between these machined surfaces were eliminated by means of copper ring gaskets (about 0.02 in. thick) coated with graphite–oil paste. Each end plate was tapped and threaded for an inlet or outlet pipe (1 in. black iron), and tapped for two thermocouple wells.

The thermocouple wells were 3 ft. lengths of $\frac{1}{4}$ in. black iron pipe, closed at one end, and attached at the other end to the end plates by means of lock nuts. That is, two thermocouple wells extended from each end throughout half the length of the reactor (R). One of each pair of wells was parallel to the inner wall of the reactor and about $\frac{1}{2}$ in. distant from it, and the other pair of wells were placed halfway between the outer surface of the central 1 in. pipe (H_1) and the inner surface of the reactor.

The reactor (R) was supported at a downward slope of 45° and attached at the upper end to the preheater (P) outlet and at the lower end to the condenser (C_1) system. The reactor contained approximately 50 lb. Alcoa Activated Alumina (Grade F–1, 4 to 8 mesh).

Electrical heating was applied externally in the following manner. Nine transite strips, $1\frac{1}{4}$ in. wide and 6 ft. long were set along the reactor (R) and evenly spaced about its circumference. Numerous slits of the correct pitch were cut in these strips, and chromel A wire wound onto these slits and about the reactor. Four separate heating zones were wound; the upper two were 1 ft. in length and the lower two about 2 ft. long. Each heating zone consisted of two heaters in parallel, i.e., wound on alternate slits in the transite strips. Each of the 1 ft. heaters was approximately 800 w. (220 v.) and the 2 ft. heaters were approximately 1500 w. (220 v.).

The amounts of heat applied to the various zones could be varied independently and over the complete range from zero to the maximum wattages stated above. Either 110 or 220 v. could be used, and either one heater or the two in parallel. In addition, each pair of heaters was connected in series with rheostats.

The wattages of the vaporizer (V), preheater (P), and oil line (H) heaters were also separately controlled by rheostats.

Temperature Measurement

Temperatures were measured by means of chromel–alumel thermocouples (*tc*) (B & S 14 gauge) and read directly on a Hoskins high-resistance pyrometer. Two-hole high temperature thermocouple insulators proved very satisfactory. Thermocouples were movable throughout the lengths of their respective wells so that temperatures of all parts of the apparatus could be obtained.

Insulation

Heated parts of the apparatus were insulated with Johns–Manville pipe covering, Supercel, Asbestosponge, or Magnesia, while irregular parts of the apparatus were insulated with rock wool.

Condenser System and Liquid Receiver

The condenser system consisted of a water-cooled iron condenser (C_1) attached to the bottom end plate of the reactor (R) and supported at a downward slope of 45°, followed by two upright water-cooled Pyrex Allihn condensers (C_2) (24 in. long) in parallel. The inner tube of the metal condenser was $\frac{1}{2}$ in. pipe, 24 in. long, while the outer was $1\frac{1}{4}$ in. pipe.

The liquid receiver (L) was a five liter Pyrex flask, fitted with one glass tube extending to the bottom of the flask (for emptying the flask by suction) and a second glass tube leading to a mercury manometer.

Dimethyl Ether Recycling System (*E*)

Galvanized pipe ($\frac{1}{2}$ in.) led from the tops of the upright Pyrex condensers (C_2) to the gas circulating pump (P_E), then to a rotameter (r_2), and finally to the vaporizer (V). A Pyrex trap close to the suction side of the pump (P_E) removed liquid which had passed through the condenser system (C_2), and a similar trap on the pressure side of the pump (P_E) protected the rotameter (r_2) from pump oil. Glass to pipe connections were made with thick-walled rubber tubing.

The pump (P_E) was a rotary vacuum type manufactured by W. C. Wood Co. Ltd., Guelph (for use with a milking machine). The rate of circulation of this pump was controlled by a by-pass and a gate valve, and indicated on a rotameter (r_2), (Schutte and Koerting No. 3–$\frac{1}{2}$ in.). The pressure of this part of the gas recycling system was read on a mercury manometer and regulated by a stopcock (both beyond the rotameter (r_2) from the pump (P_E)). The amount of gas escaping from the system through this stopcock was measured by means of a wet test gas meter.

Oil Circulation System for Heat Exchange (*H*, H_1)

The oil circulation system (H, H_1) for heat exchange was installed after preliminary experiments (see below) had shown that the temperature at the center of the catalyst in the upper part of reactor (R) might rise 20° per hour

for several hours. The temperatures of other parts of the reactor were not affected so greatly; it was necessary to apply heat to the lower part of the furnace to maintain its temperature. While the heat exchanger has not entirely eliminated this initial temperature rise, it has compensated for it, and has permitted greatly improved temperature control.

Oil (Aeroshell 140) was circulated within the reactor (R) through a 1 in. extra strong black iron pipe (H_1) concentric with the reactor. A thermocouple well ($\frac{1}{8}$ in. black iron pipe, 6 ft. long closed at one end) was concentric with the 1 in. pipe (H_1).

Outside the reactor (R), the oil circulation system consisted of:

(*a*) A Yale & Towne 20-D Tri-Rotor pump (Po) with tolerances increased to permit use with hot liquids.

(*b*) A heater (maximum wattage 2100 w. at 220 v.) which surrounded a section of the oil line.

(*c*) A reservoir, open to the atmosphere, with an overflow above the level of the top of the reactor (R).

(*d*) Appropriate pipe to join these.

About three quarts of oil was required to fill the system.

Oil was pumped directly from the pump (Po) through the heated section of the oil line into the bottom of the reactor (R), then up through the 1 in. pipe (H_1) inside the reactor to the top, along through the bottom of the reservoir, thence down to the suction side of the pump (Po).

The temperature of the oil was measured by movable thermocouples as it circulated through the reactor (R) and as it emerged from the top of the reactor, and by a thermometer near the suction side of the pump (Po).

Operation of the Pilot Plant

The catalyst was regenerated, if necessary, by drawing air over it at 450° to 475°C. for approximately five hours; reactivation did not occur at temperatures about 400° to 425°C. After the reactor (R) had cooled to 275° to 300°C., the oil line (H, H_1) was filled and the circulating oil heated. The vaporizer (V) and preheater (P) were also heated, and nitrogen circulated (e.g. 0.5 c.f.m. for 30 min.) through these, the reactor, and the dimethyl ether recycling system (E) in order to displace air (which might form explosive mixtures with dimethyl ether at 275° to 300°C.).

The reactor (R) and dimethyl ether recycling system (E) were flushed next with dimethyl ether until the dimethyl ether content of the circulating gas was approximately 95%; this usually required about 30 min.

About 40% of the circulating dimethyl ether could be directed through a special by-pass situated between the pump (P_E) and the rotameter (r_2). Samples of this dimethyl ether were analyzed in a modified Orsat apparatus; dimethyl ether content was indicated by solubility in concentrated sulphuric acid.

In a typical run with oil circulation for heat exchange and an aniline feed rate of 3 lb. per hr., the temperature of the upper 12 to 18 in. of catalyst might rise 15°C. during the first hour of reaction and remain constant thereafter. For this reason, the temperature of this upper part of the reactor (R) was regulated before introduction of aniline at 15° to 20°C. below the desired reaction temperature.

Aniline was pumped by the Pulsafeeder at the desired rate into the vaporizer (V) where it was vaporized and mixed with dimethyl ether (from the cylinder and the recycling system (E)), then passed through the preheater (P) into the reactor (R). In 10 min. or less, liquid products, mainly dimethylaniline and water, appeared in the receiver (L).

The first aliquot of liquid products collected during the establishment of equilibrium reaction conditions was discarded so that the first sample analyzed would indicate the extent of reaction.

The temperature was adjusted at 295° to 300°C. and for an aniline feed rate of 3 lb. per hr., dimethyl ether was required as follows:

(*a*) from cylinder 0.23 c.f.m. (1.2 moles per mole aniline) approximately 99.5% dimethyl ether,

(*b*) recycled 0.71 c.f.m. (3.7 moles per mole aniline) approximately 95% dimethyl ether.

The pressure of the system was determined by a number of factors, including rates of addition, reaction, and recycling of dimethyl ether, etc., and was regulated by adjustment of the escape stopcock. A positive pressure was maintained throughout the system, e.g. 20 to 40 mm. mercury on the suction side of the circulating pump (P_E) and 60 to 85 mm. mercury on the pressure side of the pump (P_E). This indicated very little resistance to flow of reactants through the system.

The liquid products were removed from the receiver (L) by suction, and dimethylaniline determined as described above.

At the end of the run and for 20 to 30 min. after aniline was no longer introduced, methanol or dimethyl ether was passed over the catalyst to remove aniline derivatives, prior to regeneration.

Preliminary Pilot Plant Experiments (no Heat Exchange)

In order to test the apparatus, a number of preliminary pilot plant runs of two to four hours' duration were carried out, in general, as described above, but prior to the installation of the heat exchange system (H, H_1). At aniline feed rates of 2 lb. per hr. or higher, the temperatures of the central upper 12 to 18 in. of the catalyst continued to rise 10° to 20°C. per hour, while the temperatures of other parts of the catalyst might rise 0° to 5°C. per hour. At aniline feed rates less than 2 lb. per hr. or in runs where the liquid charge contained approximately 90% dimethylaniline, a small amount of heat was

applied to maintain temperatures. The reaction temperature was usually 275° to 300°C., but it was difficult to determine optimum temperatures under such uncontrollable conditions. The products contained 97 to 99% dimethylaniline and rearrangement products were absent, or present in small amount only.

These experiments indicated that some form of heat exchanger was required so that: (*a*) the optimum capacity of the pilot plant (3 to 4 lb. aniline per hr.) could be realized, and (*b*) temperatures throughout the reactor would be reasonably uniform.

Pilot Plant Experiments Using Heat Exchanger (H, H_1)

The general operation of the pilot plant and the oil circulation system for heat exchange (H, H_1) have been described above.

In some early experiments, leakage of dimethyl ether from the system occurred, and the gas recycled contained air. However, considerable reaction (e.g. 75%) occurred even when the dimethyl ether content had dropped to 65% or less. When this product (approximately 75% methylation) was passed a second time over the catalyst even under these unfavorable conditions, high grade material (99% dimethylaniline) resulted. In cases of excessive leakage of dimethyl ether, the gas recycled was mainly air. Oxidation then occurred, and temperatures at the top of the reactor might rise 100°C. in 10 min. and 175°C. in 20 min. The catalyst was badly discolored, but reactivation restored its activity almost completely.

When air was excluded from the apparatus, aniline introduced at 3 or even 4 lb. per hr. yielded a product of 98 to 99% dimethylaniline.

Seven Day Pilot Plant Run

(*a*) *Normal Operating Conditions*

In order to determine the life of the catalyst Alcoa Alumina F–1, % yields of products and by-products, the effect of variation of reaction conditions, the efficiency of the heat exchange system, etc., the pilot plant apparatus was operated continuously for one week with an aniline input of 3 lb. per hr.

During this period, about 500 lb. aniline was converted to dimethylaniline, using about 325 lb. dimethyl ether. The dimethyl ether was 99.6 to 99.7% soluble in concentrated sulphuric acid and specifications indicated impurities of less than 0.2%. These impurities present in a full cylinder concentrated as the dimethyl ether was evaporated. Alcoa F–1 Alumina (49 lb.) was used.

Operating conditions, except as specified below ((*c*) Abnormal Operating Conditions) were as described previously, i.e. (*a*) catalyst temperature 295° to 300°C. (except for a section about 2 ft. from the top at 305°C.), (*b*) introduction into the catalyst of 4.9 to 5.0 moles approximately 95% dimethyl ether per mole of aniline. About 1.2 moles ether per mole of aniline was consumed, and added continually to the system, while the excess 3.7 to 3.8 moles was continuously recycled.

Dimethyl ether analyses of the circulating gases were carried out every hour or as required. Liquid samples (temperature 42°C.) were removed every one and one-half hours; aliquots were dried and distilled, and their refractive indices determined.

Temperature control was very nearly automatic, after the temperature rise at the upper end of the reactor during the first hour of aniline addition.

Refractive indices of the liquid product varied by less than ± 0.0001 from that of pure dimethylaniline throughout the week, despite the variations in the refractive indices of the aniline samples reacted (e.g. η_D^{20} 1.5839 to 1.5858).

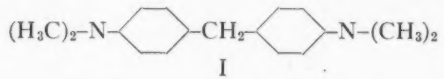
(*b*) *Quantitative Analyses of Reactions*

About halfway through the run, further proof of the quantitative nature of the reaction was obtained during a nine hour period. The weight of aniline introduced and the weight of dimethylaniline in the product were determined. The yield of dimethylaniline based on aniline was 100%, i.e. quantitative, within the limits of experimental error.

The procedure was as follows: The liquid products from this nine hour period (about 40.5 lb.) except that material removed as aliquots for dimethylaniline analyses were separated into water and dimethylaniline layers, after the addition of a weighed quantity of sodium chloride. Methanol, water, and dimethylaniline were determined for each layer. Methanol and water were separated by fractional distillation; dimethylaniline was separated from methanol and water, and from higher boiling materials by a low-plate column or by simple distillation.

Approximately 31% of the water layer and 1% of the dimethylaniline layer consisted of methanol.

The dimethylaniline contained negligible amounts of rearrangement products (due to nuclear as well as N-methylation) but 4,4′-*bis*-dimethylaminodiphenylmethane (I) (about 0.25% based on dimethylaniline) was isolated from the higher boiling residue from the dimethylaniline distillation. This residue



I

formed less than 0.5% of the dimethylaniline layer.

The structure of I was proved by synthesis (1) (warming dimethylaniline, formalin, and hydrochloric acid (25%) at 100°C. for four hours), and confirmed by mixed melting point (87° to 88°C.).

Approximately 1.2 moles dimethyl ether was added continuously per mole of aniline converted to dimethylaniline. During the nine hour quantitative period (above), about 4.4 lb. dimethyl ether in excess of the theoretical

(13.2 lb.) was consumed. This excess dimethyl ether was: (*a*) hydrolyzed to methanol (1.6 lb.); (*b*) eliminated through the escape stopcock (1.6 lb.); or (*c*) dissolved in the liquid products (1.2 lb.).

On the basis of per cent dimethylaniline in the liquid products (consistently 98 to 98.5%), the activity of the catalyst did not markedly decrease during the seven day run.

(*c*) *Abnormal Operating Conditions*

After the middle of the sixth day, reaction conditions were varied as follows. The temperature of the upper foot of catalyst was allowed to decrease about 10°C., and during a period of about nine hours, the dimethylaniline content decreased 1 to 1.5%.

The temperature was then elevated about 20°C. during a period of about nine hours. The dimethylaniline contents of distilled aliquots increased to the earlier value of about 98.5%, and the refractive indices decreased about 0.0001, probably owing to rearrangement products resulting from the higher reaction temperatures.

During the last few hours of the run, the escape stopcock for regulation of pressure was closed and the pressure in the system maintained at about the usual level by reducing the dimethyl ether introduced from the cylinder. After about three hours the dimethyl ether content of the recycled gas had decreased from 91 to 61.5%, and the rate of recirculation from 0.79 to 0.43 c.f.m. Although only about one-half the usual amount of dimethyl ether was present in the system, the dimethylaniline content of the liquid product decreased only about 1% to approximately 97%.

The nature of the gas other than dimethyl ether being recycled is not known; however it is not carbon dioxide. Since the presence of appreciable quantities of this gas for considerable periods of time was not particularly detrimental, and since its accumulation could be readily prevented under normal operating conditions, its identity was not investigated further.

Conclusion

On the bases of yields and purity of products, catalyst life, etc., this process should be suitable for the large-scale manufacture of dimethylaniline.

Acknowledgment

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EXTRACTION OF ALGINATES FROM CANADIAN SEAWEEDS[1]

By R. C. Rose[2]

Abstract

Five abundant Canadian seaweeds, *Laminaria digitata*, *Nereocystis luetkeana*, *Macrocystis integrifolia*, *Ascophyllum nodosum*, and *Fucus vesiculosus*, were rated, from a chemical standpoint, in the above order of decreasing suitability as sources of alginate; the first three species are apparently equal to seaweeds that are being used commercially elsewhere. The yield and quality of alginate were sensitive to the method and conditions of extraction and purification. The method adopted included pretreatment of the dried seaweed for 30 min. in lime water at 60°C. and for 30 min. in cold 0.2 *N* sulphuric acid. The residue was then digested in 3% sodium carbonate for two hours at 20°C. to dissolve the alginate, diluted to aid filtration, stirred for a minimum of two hours, and filtered. The solution was bleached with sodium hypochlorite and the alginate precipitated with calcium chloride. Lime pretreatment facilitated bleaching and improved the viscosity and clarity of the alginate.

Introduction

Several species of alginate-bearing weeds are abundant in Canada, but no critical, comparative study of them as sources of alginate has been made. Prerequisites of such a study are satisfactory methods of extracting, purifying, and testing alginates. The literature on preparing alginates is confined mainly to patents (7), which give no information on the effects of altering the conditions. In one patent the seaweed is first washed in 1% calcium chloride to remove nonalginate constituents but the methods usually consist of soaking the seaweed in dilute mineral acid (this step is omitted in some patents), extracting the alginate with sodium carbonate solution (which is hot in some specifications and cold in others), separating the solution from the residue, decolorizing the solution by bleaching or adsorption, and precipitating the alginate with mineral acid or with calcium chloride. When calcium chloride is used, the calcium alginate is extracted with mineral acid to produce alginic acid. The resulting alginic acid is usually converted to sodium alginate. A method of extracting alginates for estimation is available (4), but it does not include decolorization nor is it concerned with the properties of the alginate.

One property of sodium alginate that is frequently mentioned in technical literature is the viscosity of its aqueous solutions. Sodium alginate exhibits the well known electroviscous effect, but when this is swamped (by using 0.1 *N* sodium chloride as the solvent) there is a close relation between intrinsic viscosity and degree of polymerization (5).

The object of this investigation was to develop a laboratory method of preparing purified sodium alginate and to evaluate different species of alginate-bearing Canadian seaweeds.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 4 of the Associate Committee on Seaweed Research and as N.R.C. No. 2285.

[2] *With the technical assistance of J. L. Labelle.*

Experimental

Materials

The Canadian seaweeds used were *Macrocystis integrifolia* and *Nereocystis luetkeana* from the Pacific Coast and *Ascophyllum nodosum*, *Fucus vesiculosus*, and *Laminaria digitata* from the Atlantic Coast. The Pacific Coast weeds had been air-dried prior to shipping; the others were shipped wet by express (they arrived in a fresh condition) and dried at 40°C. All samples were ground in a Wiley mill to pass a 2 mm. screen.

Commercial alginate samples and ground *Laminaria Cloustoni* stems were obtained from Britain.

Estimation of Alginate and Its Viscosity in Solution

Alginate can be estimated by precipitation with calcium chloride, conversion to alginic acid, addition of excess alkali, and back titration (4). The resulting solution contains salt from the excess alkali. For viscosity measurements the amount of salt has to be controlled and, although the salt from the excess alkali can be allowed for, direct titration with alkali seemed preferable.

To study titration, 250-gm. portions of a 0.4% solution of a commercial sodium alginate (83% dry matter) were run through a tap funnel into 25 ml. of 25% calcium chloride. The precipitated alginate was filtered off, with gentle suction, in a coarse fritted glass funnel, pressed, and extracted with cold (below 15°C.) 0.5 *N* hydrochloric acid until the leachings were calcium free, and then with cold distilled water until the leachings were chloride free. As alginic acid hydrolyzes slowly, leaching time was kept to a minimum, about 30 min. The resulting alginic acid was rinsed into a weighed Waring Blendor jar which had only one flat blade (to reduce splashing) and titrated, and simultaneously dissolved, with 0.1 *N* sodium hydroxide using phenolphthalein as the indicator. The amount of sodium alginate was calculated from the titration, taking the equivalent weight of sodium alginate as 198 (6). The solution was diluted to 0.25% sodium alginate by weight; an aliquot was used for dry matter determinations, and another aliquot was made 0.1 *N* with respect to sodium chloride and its viscosity measured at 25°C. in a Fenske viscometer.

Triplicate determinations gave titration values of 41.8, 42.0, and 41.9 ml.; drying the resulting solutions at 80°C. *in vacuo* gave concentrations of 102.5, 102.5, and 102.2% of the values calculated from the titrations; and viscosities of the solutions were 7.25, 7.20, and 7.35 centistokes. To check recovery the same alginate was successively precipitated, leached, and redissolved three times. The titration values were 41.9, 41.7, and 41.3 ml. and the viscosities were 7.52, 7.35, and 7.30 centistokes; these variations are not appreciably greater than the variation among the triplicate determinations reported previously.

Extraction and Bleaching of Alginate

Preliminary tests in which various species of seaweed were extracted with alkali, either with or without first extracting with acid, showed that *Macrocystis integrifolia*, *Ascophyllum nodosum*, and *Fucus vesiculosus* gave dark colored alginate solutions which were difficult to bleach. Pretreatment of the seaweed with hot lime water eliminated much of the coloring matter. Accordingly, sodium alginate solutions were prepared for bleaching tests by stirring 60 gm. of seaweed into 600 ml. of boiling lime water and holding the mixture at 90°C. for 10 min., draining it, stirring in 600 ml. of 0.2 *N* sulphuric acid at 20°C. for two hours (4), draining it again, adding 18 gm. of anhydrous sodium carbonate, making to 600 gm. with water and keeping it at 50°C. for two hours, then diluting it to 4000 gm. and stirring overnight, and finally centrifuging and filtering.

To study bleaching, aliquots were brought to the required temperatures, sodium hypochlorite solution was added and after the required time the alginate was precipitated with calcium chloride. When no antichlor was used and hypochlorite was present, adding hydrochloric acid, to liberate free alginic acid, released free chlorine as well and the viscosity of the alginate was reduced. When sodium bisulphite was added to the alginate solution prior to the precipitation, the viscosity of solutions in 0.1 *N* sodium chloride decreased and then increased with increasing amounts of bleach. A satisfactory method of eliminating excess chlorine was to precipitate and drain the alginate and then flood it with sulphur dioxide solution. Subsequent to treatment with hydrochloric acid the color of the alginic acid was observed and recorded. The alginic acid was dissolved as previously described.

In studying alkali treatment the lime and acid treatments described previously were given to 60 gm. samples of seaweed which were subsequently drained and subdivided into four lots. This assured that pretreatment was identical within each series. The portions were subjected to varied alkali treatments and then bleached in accordance with the results of the previous study.

In some patent specifications, alginate is extracted by heating seaweed in alkali without any previous acid treatment. This method was tested by mixing 10.0-gm. portions of *L. Cloustoni* stems with 3.0 gm. of anhydrous sodium carbonate, adding 90 ml. of hot water, digesting the mixture at the desired temperatures for various times, and subsequently diluting it, etc.

To study acid treatment, 60-gm. samples of seaweed were treated with lime water, drained, and subdivided into four portions. Lime treatment was studied using 15-gm. samples.

Finally, to test the methods and to obtain information on different seaweed species, each species available was analyzed as follows: by direct alkali digestion, by lime treatment followed by alkali digestion, by acid treatment followed by alkali digestion, and by lime treatment followed by acid treatment and alkali digestion.

Results and Discussion

The effects of varying the conditions of extracting and bleaching the alginate are shown in Tables I to V; the analyses of different species are shown in Tables VI and VII. Table VI suggests that the lime–alkali method is the mildest treatment consistent with good recovery. The procedure recommended is as follows: Ten grams of milled weed is treated at 60°C. for 30 min. with about 200 ml. of water containing 0.5 gm. of calcium hydroxide, drained, and rinsed well with cold water. It is then stirred with about 200 ml. of 0.2 *N* sulphuric acid at 20°C. for 30 min. and drained again. Three grams of anhydrous sodium carbonate and sufficient water to make the weight to 100 gm. are added, mixed thoroughly, and held for two hours at 20°C. The mixture is then diluted to 1000 gm., stirred for two hours or longer at room temperature, and then centrifuged and filtered. Aliquots of 250 gm. are bleached at 20°C. for 30 min. using the least amount of bleach needed to give a white alginic acid and a constant (with increasing bleach) titration value. The bleached alginate is precipitated by running the solution slowly, with stirring, into 25 ml. of 25% calcium chloride, then drained in a fritted glass funnel, pressed, and

TABLE I

BLEACHING OF SODIUM ALGINATE SOLUTIONS WITH SODIUM HYPOCHLORITE

(250-gm. aliquots of *N. luetkeana* stem alginate solution brought to desired temperature, bleach added, solution held at constant temperature for desired time, and alginate then precipitated)

Bleach, ml. of *N* sodium hypochlorite	Bleaching time, min.	Bleaching temp., °C.	Color of alginic acid	Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes
Nil	—	—	Dark	37.0	14.9
Nil	—	—	Dark	37.1	—
Effect of amount of bleach					
0.5	30	20	Light	35.8	12.2
1.0	30	20	White	35.3	10.2
2.5	30	20	White	35.1	7.3
5.0	30	20	White	35.2	5.1
10.0	30	20	White	35.2	4.2
Effect of bleaching time					
5.0	15	20	White	35.3	7.0
5.0	30	20	White	35.2	5.1
5.0	60	20	White	35.1	4.9
Effect of bleaching temperature					
10.0	30	10	White	35.4	5.6
10.0	30	20	White	35.2	4.2
10.0	30	30	White	35.0	2.2

TABLE II

ALKALI TREATMENT OF *N. luetkeana* STEMS AFTER LIME AND ACID TREATMENT

(With each series of four the lime and acid treatment was identical. For bleaching, 1.0 ml. of *N* sodium hypochlorite was added to 250 gm. of extract)

Sodium carbonate, gm.	Digestion time, hr.	Digestion temp., °C.	Extraction time, hr.	Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes
Effect of extraction time					
4.5	2.0	20	0.5	35.6	4.4
4.5	2.0	20	1.0	36.7	4.5
4.5	2.0	20	2.0	36.3	4.3
4.5	2.0	20	16–20	37.3	4.3
Effect of digestion temperature					
4.5	2.0	20	16–20	36.4	6.2
4.5	2.0	40	16–20	36.4	5.9
4.5	2.0	60	16–20	36.6	5.2
4.5	2.0	80	16–20	36.6	4.7
Effect of digestion time					
4.5	0.5	20	16–20	34.4	8.8
4.5	1.0	20	16–20	34.4	9.1
4.5	2.0	20	16–20	36.7	9.7
4.5	4.0	20	16–20	36.5	9.5
Effect of sodium carbonate					
1.5	2.0	20	16–20	31.8	8.9
3.0	2.0	20	16–20	36.9	8.9
4.5	2.0	20	16–20	36.8	8.5
6.0	2.0	20	16–20	36.6	8.5

TABLE III

ALKALI DIGESTION OF *L. Cloustoni* WITH NO PRETREATMENT

(10.0 gm. weed digested with 3.0 gm. anhydrous sodium carbonate and 90 ml. water)

Digestion time, hr.	Digestion temp., °C.	Bleach, ml. of *N* sodium hypochlorite	Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes
1.0	60	2	28.7	10.4
0.5	80	2	35.3	12.8
1.0	80	2	35.8	13.4
1.0	100	4	35.8	4.5
2.0	100	5	35.0	3.4

TABLE IV

ACID TREATMENT OF *N. luetkeana* STEMS AFTER LIME TREATMENT

(Acid treatment followed by alkali digestion, etc., and 1.0 ml. of *N* sodium hypochlorite added to 250 gm. of each extract)

Acid treatment		Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes
Time, hr.	Temp., °C.		
Effect of time			
0.25	20	34.3	15.0
0.5	20	36.4	17.5
1.0	20	36.4	14.0
2.0	20	35.5	11.1
Effect of temperature			
0.5	10	35.7	19.3
0.5	20	36.4	16.0
0.5	30	36.0	10.8

TABLE V

EFFECT OF TIME AND TEMPERATURE OF LIME TREATMENT

(15-gm. samples treated with 200 ml. of water containing 0.5 gm. of calcium hydroxide, then acid treated, alkali extracted, etc.)

Temp., °C.	10 min. treatment			30 min. treatment		
	Bleach, ml. of *N* sodium hypochlorite	Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes	Bleach, ml. of *N* sodium hypochlorite	Titration, ml. of 0.1 *N* sodium hydroxide	Viscosity, centistokes
N. luetkeana stems						
40	2	36.2	12.7	1	37.8	29.8
60	2	37.3	11.2	1	37.9	22.8
80	1	42.9	20.1	1	39.9	13.4
100	1	38.5	13.5	1	38.9	8.6
A. nodosum						
40	—	—	—	8	24.7	5.8
60	—	—	—	3	25.4	9.1
80	5	26.3	5.8	3	25.6	8.6
100	4	26.3	5.2	2	25.8	7.6

TABLE VI

ANALYSES OF SEAWEED BY FOUR METHODS

Method 1. Direct alkali digestion at 80°C. for one hour.
2. Lime treatment, then alkali digestion at 80°C. for one hour.
3. Acid treatment, then alkali digestion at 20°C. for two hours.
4. Lime treatment, acid treatment, alkali digestion at 20°C. for two hours.

Recommended procedure used throughout except when 4.5 gm. of sodium carbonate was used with *L. Cloustoni*.
Bleach, ml. of *N* sodium hypochlorite; titration, ml. of 0.1 *N* sodium hydroxide; viscosity, centistokes.

	Method 1			Method 2			Method 3			Method 4		
	Bleach	Titration	Viscosity	Bleach	Titration	Viscosity	Bleach	Titration	Viscosity	Bleach	Titration	Viscosity
A. nodosum	20	15.4	2.4	10	27.2	6.1	15	23.3	4.2	3	25.4	9.1
F. vesiculosus	25	7.6	—	10	18.3	2.4	15	12.4	3.6	3	16.4	6.6
L. digitata	2	27.6	8.8	0.5	28.7	6.7	2	28.0	10.3	0.5	28.5	11.7
M. integrifolia	7	31.9	4.6	3	29.6	4.5	5	30.1	5.5	2	29.1	6.8
N. luetkeana stems	5	27.4	7.1	1	29.1	7.0	5	28.5	11.6	1	29.3	22.8
N .luetkeana fronds	3	21.9	11.1	2	25.3	5.8	2	23.8	14.4	0.5	23.0	18.3
L. Cloustoni	3	35.1	8.1	3	27.6	—	2	20.7	11.5	2	25.0	6.7
With 4.5 gm. sodium carbonate and water to 150 gm.	3	34.2	8.0	3	30.5	4.2	2	28.2	9.5	3	32.6	7.1

TABLE VII

YIELD AND PROPERTIES OF ALGINATES FROM DIFFERENT SPECIES

(Lime–acid–alkali method)

Species	Alginate yield*	Bleach**	Viscosity, centistokes†	Clarity††
A. nodosum	20.1	0.21	9.1	Fair
F. vesiculosus	13.0	0.33	6.6	Poor
L. digitata	22.6	0.03	11.7	Excellent
M. integrifolia	23.0	0.12	6.8	Good
N. luetkeana stems	23.2	0.06	22.8	Good
N. luetkeana fronds	18.2	0.04	18.3	Good
L. Cloustoni	27.4†††	0.15†††	8.0†††	Good

* *Expressed as per cent sodium alginate on weight of air dry weed.*
** *Expressed as gm. chlorine per gm. sodium alginate.*
† *Of 0.25% sodium alginate in 0.1 N sodium chloride solution.*
†† *Observed on solutions used for viscosity measurements.*
††† *By direct digestion method.*

flooded with dilute sulphur dioxide solution. It is then extracted with cold 0.5 *N* hydrochloric acid until calcium free, and with cold distilled water until chloride free. The alginic acid is examined visually for color and then titrated, while being stirred in a Waring Blendor, with 0.1 *N* sodium hydroxide, using phenolphthalein as the indicator. The titration value (ml.) multiplied by 0.0198 equals the sodium alginate in 250 gm. of extract; the total yield is obtained by multiplying this value by four. The titrated solution is diluted

to 0.25% sodium alginate, made 0.1 *N* with respect to sodium chloride, and the viscosity measured at 25°C. in a Fenske viscometer.

With some of the species examined certain steps of this method were omitted without seriously affecting the results and obviously with these species such steps would be omitted in commercial practice. With other species all steps were essential. To get maximum viscosities the lime treatment and bleach should be varied to suit the sample of seaweed.

A detailed examination of the results shows that small amounts of hypochlorite reduced the titration value; larger amounts had little added effect (Table I). The loss of titratable material may suggest that unbleached alginate contains an acidic impurity which is easily oxidized. Viscosity is obviously sensitive to hypochlorite. In Table II the viscosity differences among the series must be attributed to variations in the lime and acid treatments. The digestion temperature recommended, 20°C., was sufficient, as higher temperatures did not increase the yield. When no pretreatment was given (Table III) a digestion temperature of 80°C. was necessary. Acid treatments longer, or at a higher temperature, than recommended, decreased the viscosity (Table IV). Lime treatment for 30 min. at 40°C. was sufficient to reduce the bleach needed with *N. luetkeana* stems to 1 ml. but 60°C. was necessary with *A. nodosum* (Table V). Other tests with *A. nodosum* showed that successive lime treatments were no more effective than a single treatment in reducing the bleach required. Lime treatment effectively reduced the bleach needed by each Canadian species and acid treatment reduced the bleach needed by the darker species (Table VI). It also improved filtration and clarity of extracts. Lime treatment did not affect the color of extracts of *L. Cloustoni* but this species, unlike the others, had been weathered during outdoor drying and this may have removed coloring substances.

The yield (titration value) from most species was almost independent of the method of extraction (Table VI) but *A. nodosum* and *F. vesiculosus* failed to respond to direct digestion. This may have been due to impurities that interfered and that were destroyed or removed by lime treatment. The yields (recalculated on a dry basis) obtained from *L. digitata*, *A. nodosum*, and *F. vesiculosus* were similar to those reported on samples of these same species collected in Scotland (1, 2, 3). The yield from *L. Cloustoni* was highest by direct extraction (Method 1, Table VI). Increasing the amount of sodium carbonate increased the yield by the other methods but not to the value obtained by direct extraction. Neither regrinding the sample nor further increasing the amount of sodium carbonate had any effect.

From a commercial standpoint the value of any sample of seaweed as a source of alginate depends upon its alginate content, the relative cost of extracting the alginate, and the quality of the alginate. The alginate contents of the Canadian species studied varied from 13% to 23% (Table VII). The top value is lower than that of a commercial sample of *L. Cloustoni* but the

importance of this cannot be assessed unless relative costs of harvesting and drying are also known. The high value of *L. Cloustoni* may be due to loss of nonalginate dry matter during weathering.

The cost of extracting alginate depends on chemical costs and operational costs. In these laboratory tests the amount of chemicals, other than bleach, was fixed and therefore varied, on a yield basis, inversely as the yield. In practice, however, chemical consumption would be adjusted within limits, according to the alginate content of the weed, and variations per ton of alginate would be minor. On the other hand the consumption of bleach varied widely and this would reflect on the cost of alginate from different species. Operational costs, particularly filtration costs of seaweed extracts, cannot be assessed on a laboratory scale but, in general, lower yields suggest higher amounts of insoluble weed residue that have to be removed.

Quality of alginate depends upon color, purity, and viscosity as well as on factors such as shelf life (odors may develop during storage and viscosity may drop). The color of preparations from all species was satisfactory. The clarity of the 0.25% solutions prepared for viscosity determinations varied widely. Although the amount of insoluble impurities is reduced by lime treatment and by filtration, some species gave much clearer solutions than others under comparable conditions. *L. digitata* rated highest; *N. luetkeana* and *M. integrifolia* were equal to *L. Cloustoni* but *A. nodosum* and *F. vesiculosus* were inferior.

On viscosity the samples rated, highest to lowest, *N. luetkeana*, *L. digitata*, *A. nodosum*, *L. Cloustoni*, *M. integrifolia*, and *F. vesiculosus*. Experience has shown that alginate in seaweed remains highly polymerized provided the weed does not rot, and also during low temperature drying; consequently the varied methods of shipping and drying the weed used in these studies probably did not affect the above order.

If bleach, viscosity, and clarity are considered together then these species could be rated, in decreasing order of suitability as sources of alginate, *L. digitata*, *N. luetkeana*, *L. Cloustoni*, *M. integrifolia*, *A. nodosum*, and *F. vesiculosus*. From a commercial standpoint *A. nodosum* appears marginal and *F. vesiculosus* unacceptable. More results, based on samples harvested by practical methods, are needed before final conclusions can be drawn but it is undoubtedly significant that the alginate industries in Eastern U.S.A., Britain, and Norway are based on *Laminaria* species (despite the abundance of other species) and the industry in Western U.S.A. is based on *M. pyrifera*.

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STUDY OF THE COPOLYMERIZATION OF BUTADIENE AND STYRENE IN EMULSION AT SUBFREEZING TEMPERATURES[1]

By R. J. Orr[2] and H. Leverne Williams[3]

Abstract

The characteristics of the copolymerization of butadiene and styrene in emulsion have been studied at −18°C. and −10°C. Polymerization charge recipes have been developed which should permit commercial production at these temperatures at rates comparable to those used at 50°C. The effect of different variables on the rate has been determined. Methanol was a satisfactory antifreeze agent. Potassium hydrogenated fatty acid soap or hydrogenated rosin soap was a suitable emulsifying agent. The latter had to be used in a so-called "methanol first" technique. The pH of the emulsifier had to be adjusted with care. Mixtures of the two soaps were particularly good. Electrolytes as viscosity reducing agents retarded the reaction at low conversion but caused a higher conversion over all. Para substituted cumene hydroperoxides were compared with the result that improved performance was obtained as the para substituent became more electropositive. Activators for the redox system were found to be best, when composed of a carefully chosen combination of ferrous sulphate, arsenious oxide, potassium pyrophosphate, and tetrasodium ethylenediamine tetraacetate.

Introduction

General purpose chemical rubbers are currently produced by a free radical process in aqueous emulsion. It has been established that by lowering the temperature at which this reaction is carried out the properties of the polymer (11) and the latex (12) so produced are considerably improved. Several studies (1, 4, 5, 6, 7, 9, 16) indicate that this is due to greater regularity in the molecular chain and perhaps to a more uniform molecular weight and molecular chemical structure.

Present commercial production of these "cold rubber" types takes place at a temperature of 5°C. to 10°C. Any further significant decrease in the polymerization temperature takes the reaction to subfreezing temperatures. In this region many new problems present themselves. The introduction of an antifreeze may alter the properties of the emulsion and in some cases the antifreeze possesses functional groups which may affect the rate of polymerization. The type of emulsifier which will give rise to a favorable rate of reaction at above freezing temperatures may not be satisfactory at lower temperatures. The conditions to which the aqueous phase must be subjected for good reaction conditions may vary with decreasing temperature. The commonly used catalyst, cumene hydroperoxide, may not be satisfactory at lower temperatures. The usual ferrous sulphate – potassium pyrophosphate activator has proved satisfactory at 5°C. but other sequestering agents have

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been developed which might give rise to more suitable rates at subfreezing temperature.

It was thus of interest to develop practical recipes and to study further the properties of the polymers produced. Some of the recipes used in the previous studies (see also (8)) seemed to be unsuited for this purpose either because of slow reaction time or because of unsuitable emulsifier type.

Experimental Techniques

The experiments were carried out in 8 oz. peroxide bottles with punctured metal screw caps in which the fiber gasket was replaced by a double rubber gasket consisting of an outer oil resistant Koroseal* sheet and an inner self-sealing Butyl** gasket prepared from undercured unpigmented sheets. Initial difficulty was encountered when the Koroseal tended to harden under prolonged exposure to low temperature and to resist puncture by syringe needles. This was overcome by storing the Koroseal in styrene and cutting the gaskets immediately before use.

The standard charging procedure was to add the antifreeze to the bottle, followed by the emulsifier dissolved in the water, then the mercaptan used as modifier dissolved in the styrene, and finally the butadiene. A small excess of butadiene was added to the bottle and allowed to evaporate to the desired weight at which time the bottle was securely capped. By this method, all residual oxygen was swept from the bottle and the experiment was conducted under reasonably oxygen-free conditions. The bottles were then clamped in the constant temperature bath and rotated end over end for 30 min. in order to bring the contents to bath temperature and to effect pre-emulsification. The activator, in water solution, and the catalyst, in styrene solution, were then added volumetrically by hypodermic syringe. After the required time the reaction was stopped by injection of the desired amount of an emulsion of 2,5-ditertiary butyl hydroquinone. Nitrogen at a pressure of 15 to 20 p.s.i. was then introduced into the bottles and a sample of latex was withdrawn by syringe. This sample was weighed, evaporated to dryness, and weighed again. From this the percentage of the monomers which had been converted to polymers could be calculated.

Polymerization Recipe

The different basic charge recipes or formulae used have been tabulated and will henceforth be referred to by number. Quantities are by parts of the pure ingredient, allowance being made for impurities, including water.

Any variation from the outline below is expressed by the number corresponding to the most similar recipe and by recording any changes made.

* *Polyvinyl chloride sheet, B.F. Goodrich Chemical Co.*
** *A product of Polymer Corporation Limited.*

	Recipe Number					
	I	II	III	IV	V	VI
Butadiene (Polymer Corp. technical)	70	70	70	70	70	70
Styrene (Polymer Corp. technical)	30	30	30	30	30	30
Water (distilled)	192	180	190	228	125	157
Methanol (du Pont synthetic)	48	37	46	55	46	46
Potassium fatty acid SF soap flakes (Swift and Co.)	5.0	4.6	5.0	6.0	5.0	2.5
Dresinate S–149 (Hercules Powder Co.)	..	..	..	..	..	2.6
Daxad 11 (Dewey and Almy)	0.02	0.02	0.10	0.10	0.10	0.05
Mixed tertiary mercaptans (Phillips)	0.24	0.24	0.24	0.24	0.24	0.24
Potassium chloride	0.15	..	..	..	..	..
Potassium sulphate	..	..	..	..	..	0.10

The activators used are similarly tabulated below.

	Activator Number			
	I	II	III	IV
Ferrous sulphate heptahydrate	0.16	0.16	0.16	0.042
Potassium pyrophosphate (anhydrous)	0.15	0.28	0.14	0.034
Arsenious oxide	0.07	....	....	0.024
Sequestrene AA*	....	....	....	0.0028

* *Ethylene dinitrilotetraacetic acid, approx. 100%, from Alrose Chemical Co.*

Experimental

I. *Investigation of Antifreeze Agents*

Four antifreeze agents were investigated; glycerine, ethylene glycol, ethanol, and methanol. Conversion rates and antifreeze properties were observed for each of these at different concentrations. As may be seen from Table I glycerine and ethylene glycol were quite effective and excellent rates of conversion were achieved. Glycerol was the better. Each acted to promote the polymerization more as the concentration of antifreeze increased.

Both, however, are costly and difficult to recover owing to their high boiling points. Ethanol proved to retard the reaction so methanol was tried. The results for both −10°C. and −18°C. are shown in Table II.

At all concentrations for which conversion rates were studied, no freezing took place. This indicates that methanol is a suitable antifreeze giving somewhat slower conversion rates than the glycerol or ethylene glycol. Similar conclusions were reached by other workers (14).

It is interesting to note that there is an optimum in the conversion rate which is not a function of polymerization temperature. This is at 46 parts of methanol under the conditions outlined above and represents a concentration of 19.4% methanol. The question arises whether the total methanol content or the methanol concentration in the aqueous phase is the factor determining

TABLE I

GLYCERINE AND ETHYLENE GLYCOL AS ANTIFREEZE AGENTS IN −18°C. POLYMERIZATION

Parts/100 monomers	% Conversion in 17 hr.	Latex appearance
*Glycerine**		
35	17.3	Solid
45	35.8	Solid
50	68.8, 26.8	Semisolid
55	59.1	Semisolid
60	79.6	Semisolid
65	77.1	Semisolid
*Ethylene glycol**		
35	44.2	Solid
45	49.2	Solid
50	38.7	Solid
55	36.6	Semisolid
60	55.6	Solid

* *Charge Recipe IV; Activator III; diisopropyl benzene monohydroperoxide, 0.15 parts.*

TABLE II

METHANOL AS AN ANTIFREEZE IN −18°C. AND −10°C. POLYMERIZATION

Parts/100 monomers	% Conversion in 17 hr.*	Parts/100 monomers	% Conversion in 17 hr.**
46	26 3	30	21.0
48	22.8	34	21.6
50	23.2	38	22.8
52	23.7	42	26.2
54	19.9	46	28.4
56	19.6	50	27.2
58	6.0		
60	6.0		

* *−18°C. Charge Recipe II; Activator III; 0.15 parts diisopropyl benzene monohydroperoxide.*

** *−10°C. Same charge recipe and activator; 0.35 parts catalyst.*

TABLE III

EFFECT ON THE −18°C. CHARGE RECIPE OF TABLE II OF VARIATION OF AQUEOUS PHASE AT FIXED METHANOL CONCENTRATION

Parts methanol/100 monomers	Parts water/100 monomers	% Conversion in 17 hr.
37.2	150	19.6
38.7	160	20.7
41.1	170	20.6
43.5	180	21.0
46.0	190	24.1
48.5	200	15.1
50.7	210	20.0
53.7	220	20.9

the optimal rate. With this in mind, the methanol concentration was held constant at 19.4% and the total amount of the aqueous phase was varied. The results are shown in Table III.

There is again an optimum at 46 parts of methanol. If the methanol concentration were the factor determining the optimal rate, then this system should show an optimal rate at 190 parts water also when the methanol content is kept constant and the water varied. The effect of variation in water content at constant methanol content (46 parts) on conversion rate was determined and is shown below in Table IV.

TABLE IV

EFFECT ON THE −18°C. CHARGE RECIPE OF TABLE II OF DILUTION OF AQUEOUS PHASE AT FIXED METHANOL CONTENT

Parts water/100 monomers	% Conversion in 17 hr.
125	28.9
135	47.5
145	54.6
160	53.3
190	12.4

There is a different optimal ratio of ingredients, at 145 to 160 parts water. Thus it is the methanol content rather than the methanol concentration which is the factor in determining the optimal rate.

II. *Study of Emulsifiers*

All previous investigations at these temperatures had been concerned with soaps which produced a polymer unsuitable for industrial use. For this reason only those soaps which were useful from commercial point of view were studied. The first type found useful in promoting satisfactory rates was a potassium hydrogenated fatty acid silica free soap flake. In Charge Recipe III with Activator III, 5.0 parts of the emulsifier, and 0.15 parts cumene hydroperoxide at −10°C., a comparison between this and two types of rosin soaps was made. Dresinate 214*, a commercial disproportionated rosin soap, yielded only 11.8% conversion in 17 hr. while Dresinate S–134*, an experimental fully hydrogenated product, gave 67.5% as compared with 61.7% for the K-fatty acid silica free soap flakes.

There is a second variable, the nature of the method by which the soap is dissolved in the aqueous methanol medium. It makes no difference whether the potassium fatty acid soap is dissolved in the water first and methanol added, or dissolved in a mixture of the two. The Dresinates must be dissolved first in the alcohol for a satisfactory rate. This is known as the "methanol first" charging process. In Charge Recipe IV with Activator IV and 0.15 parts of diisopropyl benzene monohydroperoxide at −10°C. a comparison was made between the different types of charging procedures for Dresinate S–149*,

* *Hercules Powder Company.*

a commercially available hydrogenated rosin soap. Whereas 35.9% conversion in 17 hr. was attained by the methanol first procedure, only 0.5% was attained by the water first procedure.

Still another interesting phenomenon shown by these emulsifiers is their behavior on blending. If a Dresinate S–149 solution in methanol and water is prepared by the methanol first charging procedure and is mixed with a potassium fatty acid soap solution prepared by the water first method in varying proportions so that the total emulsifier weight in the polymerization charge is always constant, the results shown in Table V may be obtained. Blending of the two soaps results in a condition which is beneficial to the rate of polymerization.

TABLE V

EFFECT OF BLENDED EMULSIFIERS ON RATE OF POLYMERIZATION AT −18°C.

Dresinate S–149 (% of total soap)	% Conversion in 17 hr.*
0	42.5
13.2	69.7
28.3	69.1
43.4	74.8
56.8	74.8
71.8	34.3
100	35.9

** Charge Recipe V; Activator IV; diisopropyl benzene monohydroperoxide, 0.15 parts; emulsifier, 5.3 parts.*

The soap concentration in the polymerization charge influences both the rate of reaction and the properties of the polymer. In attempting to improve the rate it is unwise to add too much soap, owing to the detrimental influence of the excess soap on the properties of the rubber so produced. Usually an arbitrary value of about 5.0 parts soap/100 parts monomers is chosen. With the view of increasing rate through small increases in the soap content, a survey of concentration effects was carried out using potassium fatty acid soap. This was done in two manners. The amount of water in the system was first held constant, and the soap content varied. This had the net effect of varying the soap concentration. It may be seen from Table VI that the rate shows a direct dependence on soap content for low soap concentrations.

An alternative method of varying the soap content in the system is to hold the concentration constant and vary the soap and water contents simultaneously. This results in the rate showing a much greater dependence on soap content than was shown when the water content was held constant as may be seen also in Table VI. It is possible by this means to achieve relatively large changes in rate by only small changes in the composition of the original charge.

It was discovered early in the investigation that the pH of the soap solution exerted a profound effect on the polymerization rates. This is illustrated by Table VII.

TABLE VI

INFLUENCE OF SOAP CONCENTRATION ON RATE AT −18°C.

Parts soap/100 monomers	Parts water/100 monomers	% Conversion in 17 hr.
*Constant water**		
0.8		2.0
1.0		3.6
2.5		4.0
3.3		6.2
4.2		7.3
5.0		8.5
*Constant soap concentration in aqueous phase***		
3.4	105	21.5
4.7	145	54.7
5.7	175	58.5
6.0	185	70.8

* *Charge Recipe V; Activator III; cumene hydroperoxide, 0.07 parts.*
** *Charge Recipe V; Activator IV; diisopropyl benzene monohydroperoxide, 0.07 parts.*

TABLE VII

EFFECT OF pH OF SOAP MASTER BATCH ON CONVERSION IN 17 HR.

pH	% Conversion at −10°C.*	% Conversion at −18°C.**
9.9	8.4	..
10.1	..	0
10.5	33.2	..
10.7	..	0
10.8	28.0	..
11.0	32.2	..
11.2	..	0
11.4	..	0
11.5	78.3	..
11.8	..	30.8
12.0	79.4	..
12.1	..	2.5
12.5	23.5	..
13.0	9.2	..

* *Charge Recipe III; Activator II; diisopropyl benzene monohydroperoxide, 0.35 parts.*
** *Charge Recipe IV; Activator III; diisopropyl benzene monohydroperoxide, 0.15 parts.*

While the optimal pH shows little dependence on temperature being 11.8 at both −18°C. and −10°C., the system is decidedly more sensitive to pH change at −18°C. The reason for this was investigated further at −18°C. by determining the time–conversion characteristics of the charge with soap master batch of pH 10.8. There was no conversion up to 17 hr. and only 29.0% after 100 hr. It is thus evident that the reason for low conversions at low pH is the presence of an induction period which is shortened by raising the pH of the aqueous phase. The inhibitor in this case may be small amounts of oxygen dissolved in the recipe constituents.

III. *Study of Viscosity Reducing Agents*

The methods most commonly used to make a fluid latex which will favor heat transfer are to add additional surface active or dispersing agents or electrolytes. The effect of a commonly used dispersing agent, Daxad 11, on the conversion in 17 hr. at −18° C. (Charge Recipe VI; Activator IV; diisopropyl benzene monohydroperoxide, 0.07 parts) was determined and it was evident that this material had little, if any, effect upon conversion rate. In general, its effect upon the fluidity of the latex is a function of the type of reactor used so that quantitative work of this nature in laboratory polymerizations is of little direct use. However, this agent shows considerable promise as a means of reduction of latex viscosity without decrease in rate.

The addition of electrolytes to the polymerization charge is frequently desirable since they increase the fluidity, and hence the heat transfer of the latex. The effect of a great many electrolytes on rate was evaluated at these subzero temperatures. The results are inconclusive at −10°C. In slow reactions at low conversions, all electrolytes inhibited the rate. However, at −18°C. in faster reactions and at high conversion the rate increased slightly with increasing electrolyte content. These results are shown in Table VIII.

TABLE VIII

EFFECT OF ELECTROLYTES ON −10°C. AND −18°C. POLYMERIZATION REACTIONS

Temperature	Parts electrolyte	Compound	% Conversion in 17 hr.
−18°C.*	0.0		86.0
	0.05	Na_3PO_4	89.3
	0.10	Na_3PO_4	88.5
	0.05	K_2SO_4	91.3
	0.10	K_2SO_4	91.3
−10°C.**	0.0		30.1
	0.05	K_2SO_4	28.1
	0.10	K_2SO_4	13.6

* *Charge Recipe V; Activator VI; diisopropyl benzene monohydroperoxide, 0.15 parts.*
** *Charge Recipe II; Activator I; diisopropyl benzene monohydroperoxide, 0.35 parts.*

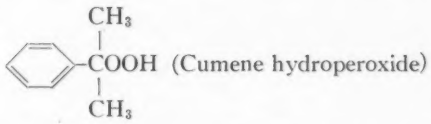
IV. *Study of Alternative Hydroperoxides*

The normal method of initiating emulsion polymerizations at low temperatures, precluding formation of free radicals by thermal or other types of decomposition, is by the following redox reaction:

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + OH^{-} + M^{(n+1)+}$$

where M is an ion or a compound with two or more oxidation states. The peroxide is usually a hydroperoxide, owing to the more rapid reactions thus resulting. The metal ion must be bound in a chelate complex. No adequate treatment of the underlying reactions for this system has yet been published

but some concepts have been advanced (15, 17). For several reasons the combination of ferrous iron and cumene hydroperoxide has been chosen for



(Cumene hydroperoxide)

commercial redox recipes. The ferrous iron is used in the form of a ferrous pyrophosphate or other complex. This is known as the "activator". In data presented later in this and the following section it is obvious that this combination becomes inadequate in promotion of satisfactory rates at subfreezing temperatures.

The first step involved substitution of cumene hydroperoxide by a more suitable hydroperoxide. Four hydroperoxides* were investigated at −18°C. These are, cumene hydroperoxide (CHP), para methyl cumene hydroperoxide (MCHP), para isopropyl cumene hydroperoxide (ICHP), and *p*-tertiary butyl cumene hydroperoxide (TBCHP). A ferrous pyrophosphate activator prepared from ferrous sulphate and potassium pyrophosphate and aged 15 min. at 60°C. was used throughout. The ferrous iron content was held constant at 0.16 parts ferrous sulphate heptahydrate and the hydroperoxide content was varied. A typical result of a series of experiments such as this may be found in Table IX.

TABLE IX

EFFECT OF CONCENTRATION OF TBCHP AT −18°C.*

TBCHP (parts)	TBCHP (moles)	Fe^{++}/TBCHP (molar)	% Conversion in 17 hr.
0.034	1.6×10^{-4}	3.5	10.6
0.068	3.3×10^{-4}	1.7	13.1
0.102	4.9×10^{-4}	1.1	20.3
0.136	6.5×10^{-4}	0.86	27.9
0.170	8.2×10^{-4}	0.68	26.1

* *Charge Recipe IV; Activator III.*

It may be seen that the overall conversion rises to a maximum value on increasing the TBCHP content. On further increase the conversion attained is decreased. This Fe^{++}/TBCHP ratio is the optimal ratio for that hydroperoxide. These optimal ratios were determined in a similar manner for the three other hydroperoxides. The data are summarized in Table X.

This shows that as the electropositive character of the *p*-substituent increases, the peroxide becomes more effective. However, the solubility in the aqueous phase diminishes in the same order** so that the solubility may be

* *These will hereafter be referred to only by the designated letters.*
** *Private communication—Hercules Powder Company.*

TABLE X

EFFECT OF HYDROPEROXIDE STRUCTURE ON REACTION CHARACTERISTICS AT −18°C.

Hydroperoxide	% Conversion in 17 hr. for optimal charge*	Fe^{++}/peroxide ratio (−18°C.) (mole)		% Conversion in 17 hr. for optimal charge**	Fe^{++}/peroxide ratio (−10°C.) (mole)**
		*	**		
CHP (Hercules)	10	0.61		20	0.22
MCHP (Hercules)	19	0.68			
ICHP (Hercules)	25	0.68–0.77	0.63	87	0.20
TBCHP (Hercules, Phillips)	28	0.86			

* *Charge Recipe V; Activator III.*
** *Charge Recipe III; Activator III.*

important. It is of interest too that the more soluble peroxides require smaller amounts of iron to achieve optimal conversion in a given time.

This solubility aspect was investigated further. Recalling that the charge recipe V used in these determinations contained 125 parts water, the effect of aqueous phase dilution was investigated by determining the optimal Fe^{++}/peroxide ratio with 190 parts water (charge recipe III). As may be seen from Table X the optimal Fe^{++}/peroxide ratio decreased (Column 3, comparison of ICHP at −18°C., * and **). If it is assumed that the aqueous phase was at all times in equilibrium with the oil phase then it appears that an increase in the absolute amount of peroxide in the aqueous phase brings about a decrease in the Fe^{++}/peroxide ratio. This might explain the variation in the different peroxides and also the temperature variation of these quantities on the basis of distribution changes with temperature. It would also appear to be possible to generalize these conclusions in saying that any factor affecting the distribution of the peroxide between the aqueous and oil phases would correspondingly affect the optimal ratios of the activator to catalyst.

It is also known that if the Fe^{++}/peroxide ratio is held constant at the optimal ratio previously determined and the total amount of both constituents varied, the conversion once more shows a maximum for a given content of these same constituents. This behavior is illustrated in Table XI for TBCHP.

TABLE XI

EFFECT OF CONCENTRATION OF TBCHP ON CONVERSION AT −18°C.*

TBCHP (parts)	TBCHP (moles)	% Conversion in 17 hr.
0.027	1.3×10^{-4}	3.8
0.054	2.6×10^{-4}	9.4
0.082	3.9×10^{-4}	16.5
0.110	5.3×10^{-4}	21.6
0.136	6.5×10^{-4}	25.9
0.160	7.7×10^{-4}	20.3

* *Charge Recipe IV; Activator III; Fe^{++}/TBCHP = 0.86.*

The data for all the hydroperoxides are summarized in Table XII.

TABLE XII

OPTIMAL FERROUS IRON – PEROXIDE – MONOMER RELATIONS AT −18°C.*

Hydroperoxide	Fe^{++}/peroxide ratio (mole)	Fe^{++}/monomer ratio at optimal conversion (mole)	Peroxide/monomer ratio at optimal conversion (mole)
CHP	0.61	3.7×10^{-4}	6.1×10^{-4}
PCHP	0.68	3.5×10^{-4}	5.1×10^{-4}
ICHP	0.70	3.5×10^{-4}	5.0×10^{-4}
TBCHP	0.86	3.6×10^{-4}	4.1×10^{-4}

* *Charge Recipe IV; Activator III.*

It is obvious that while the optimal peroxide/monomer ratio varied in the same manner as in Table XI, the Fe^{++}/monomer ratio remained approximately constant. The reason for this is not apparent but it appears that all ferrous iron contents over a certain limit, which is independent of the peroxide used, inhibit the reaction in the sense that the conversion in 17 hr. is reduced. This may be due to an altered time–conversion curve.

V. *Study of Alternative Activators*

As was previously stated (Section IV) it is necessary to use the ferrous iron in the form of a chelate. The chelate used has a large effect on the degree of conversion attained in any given time. Potassium pyrophosphate, the usual agent which has been used for this purpose proved quite inadequate, even with the "fast" peroxides previously described. It was therefore necessary to investigate other chelating agents with a view to obtaining more rapid polymerizations. It would not be practical to discuss in detail the numerous investigations required to establish activator concentrations. In Table XIII are listed the results of those studied.

TABLE XIII

A COMPARISON OF SOME DIFFERENT ACTIVATOR SYSTEMS AT −18°C.

Chelating agent	Optimal molar proportions of activator	Fe^{++}/peroxide ratio (mole)	% Conversion in 17 hr.
$K_4P_2O_7$*	$FeSO_4$: $K_4P_2O_7$	0.70	16
$[(KOOC)_2NCH_2]_2$	$FeSO_4$: 1.5$[(KOOC)_2NCH_2]_2$	1.40	29
As_2O_3			0
$K_4P_2O_7$–As_2O_3	$FeSO_4$: $K_4P_2O_7$: As_2O_3	0.70	26
$K_4P_2O_7$–$[(KOOC)_2NCH_2]_2$**	$2FeSO_4$: $K_4P_2O_7$: $[(KOOC)_2NCH_2]_2$	0.70	21
$K_4P_2O_7$–As_2O_3–$[(KOOC)_2NCH_2]_2$	$[2FeSO_4$: As_2O_3:$K_4P_2O_7]$ $[2/3FeSO_4$–$[(KOOC)_2NCH_2]_2]_3$	0.93	44–58

* *All $K_4P_2O_7$ complexes were aged 15 min. at 60°C. This gives better results than unaged material.*

** *$FeSO_4$: 1.5 $[(KOOC)_2NCH_2]_2$ at an equivalent iron content gave 2.8% conversion in 17 hr.*

The acceleration of the rate caused by the addition of arsenious oxide is not yet understood. The molar ratios of arsenious oxide and potassium pyrophosphate for that activator makeup yielding the most satisfactory rates are about 1: 1. This may indicate formation of a complex between potassium pyrophosphate, arsenious oxide, and ferrous sulphate heptahydrate which is highly effective in promoting emulsion polymerization.

The maximum rate shown by salts of ethylenediaminetetraacetic acid and potassium pyrophosphate may be due to the same cause since once again the molar ratios of the chelating agents giving rise to the maximum in the conversion in 17 hr. is approximately 1: 1. On adding arsenious oxide to the complex, the structure seems to be changed and the rate is further increased. This activator was synthesized *in situ* from two complexes—a ferrous arsenite – pyrophosphate complex and a ferrous ethylenediaminetetraacetate. The method by which the necessary ferrous iron was distributed between the two simple complexes influenced the polymerization rate greatly. It is also interesting to note that the optimal Fe^{++}/peroxide ratio varies with the sequestering agent.

A new method for synthesis of iron-free polymer has become available recently using the amine activators (10, 15, 18). Probably the most effective of these is tetraethylene pentamine. This compound was studied with a view to extending synthesis of iron-free polymers to these subzero systems. The presence of ferrous iron in any concentration was found to decrease the overall conversion quite markedly. In the absence of iron a relatively rapid reaction was obtained which showed an optimum in conversion at a pentamine/diisopropyl benzene monohydroperoxide ratio of 2.2 moles. These are shown in Table XIV.

TABLE XIV

PENTAMINE ACTIVATION AT −18°C.

Moles pentamine/ 100 gm. monomers	Moles $FeSO_4$/ 100 gm. monomers	Pentamine/hydroperoxide mole ratio	% Conversion in 17 hr.*
1.06×10^{-3}		1.38	46.7
1.06×10^{-3}	0.9×10^{-4}	1.38	25.8
1.06×10^{-3}	3.6×10^{-4}	1.38	0
1.06×10^{-3}	5.4×10^{-4}	1.38	0
1.69×10^{-3}		2.20	50.7
2.12×10^{-3}		2.75	47.5

* *Charge Recipe VI; diisopropyl benzene monohydroperoxide, 0.15 parts.*

Discussion

The major reason for the study was to devise means of preparing polymers and latex at subfreezing temperatures at practical rates. This has been achieved and in addition some recipes have been so rapid that the relatively slow heat transfer from large reactors might render temperature control difficult.

The use of antifreeze agents is necessary. The choice depends upon initial cost, effectiveness, and ease of recovery. Only methanol meets these requirements. But ethylene glycol and glycerol yield substantially faster rates of conversion. This effect may be related to the effect of sugar in conventional type recipes (10, 15) i.e. to an effect upon the rate of decomposition of the catalyst, or to an effect upon the number of soap micelles present. The necessity of the "alcohol first" technique for the rosin soaps suggests a very strong influence of the antifreeze agent upon micelle structure, which action must be somewhat less with the fatty acid soaps. There is no ready explanation of the narrow pH range for best results and such a range makes pH control difficult for commercial use.

The recipes are sufficiently rapid that electrolytes can be added to enhance the fluidity of the latex for heat transfer. Under certain conditions these electrolytes increase the rate of conversion. This must be due to an effect upon the soap micelles.

The mechanism of polymerization initiation is suspected to be formation of free radicals in the aqueous phase by reaction between the catalyst and activator after which the free radical migrates to a monomer–polymer particle (2, 3, 13, 14). The interrelationships between hydroperoxide and ferrous iron seem in agreement with these concepts in the sense that as the solubility of the hydroperoxide is diminished the optimal iron concentration is increased. Since the system is dynamic and the free iron would not be a function of the total (free and complexed) iron concentration it seems likely that the ease of rupture of the O–O bond and the activity of the resulting alkyloxy radical have altered under the influence of the para substituent. Considerably more data are required on this phase of the study.

So many variables affect the rate of conversion that an adequate discussion of the various optimal concentrations cannot be made. The final conversion is influenced by the shape of the time–conversion curve.

Having achieved these recipes considerable work is being done* on the effect of subfreezing polymerization temperatures on the comonomer reactivity ratios, the mercaptan disappearance, and the viscosity data to elucidate some of the changes in the chemical and physical heterogeneity of the polymer formed.

Acknowledgments

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A MODIFIED IODINE PENTOXIDE METHOD FOR THE DETERMINATION OF CARBON MONOXIDE[1]

By G. A. Grant, Morris Katz, and R. L. Haines

Abstract

The iodine pentoxide method for the estimation of carbon monoxide has been improved by refinements in the design of the apparatus and by the spectrophotometric estimation of the liberated iodine. The improved apparatus and methods are demonstrated by estimating the carbon monoxide concentration in 10 known mixtures of carbon monoxide and nitrogen, ranging in concentration from 0.09 to 0.0007% carbon monoxide.

Introduction

Since carbon monoxide in essence reduces the partial pressure of oxygen in the blood, concentrations that are tolerable at normal barometric pressures are dangerous at low barometric pressures. Concentrations of carbon monoxide as low as 0.01% would have no appreciable effect up to three hours' exposure at normal barometric pressure, but would be harmful to personnel at low barometric pressures. Therefore, any investigations concerning the carbon monoxide problem at high altitudes will necessitate the estimation of carbon monoxide at low concentrations. Various methods appear to be satisfactory for determining high concentrations (1, 2) of carbon monoxide, but for concentrations of the order of 0.01 to 0.0001%, these methods are not sufficiently accurate. It is, therefore, necessary to develop new techniques or to extend the accuracy of the existing ones.

Although various methods have been devised for the determination of carbon monoxide in concentrations ranging from 0.01 to 0.001% (6, 7, 10, 13, 14, 17), no one method appears to be satisfactory on small samples of gas (up to 500 ml.). From a recent survey by the National Bureau of Standards (15) of the determination of small amounts of carbon monoxide in air, the iodine pentoxide and the N.B.S. colorimetric method (14) appear to give the best results. Although the gravimetric methods (1, 13) gave good precision, large samples of gas were necessary for analysis. In any investigation where only small samples of gas are obtainable (500 ml. or less), these methods are not applicable. The N.B.S. colorimetric method (14) requires constant standardization, while the iodine pentoxide method gave good results from some laboratories and poor results from others. This would indicate that some standardization of procedure should be adopted and refinements should be made in the apparatus and technique. There are many sources of error in the iodine pentoxide method. If any moisture is allowed to pass through the

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iodine pentoxide tube, iodine is liberated; also, iodine may be absorbed by stopcock grease; and, finally, the titration of the iodine with 0.005 normal sodium thiosulphate solution does not produce a distinct end point when low concentrations of carbon monoxide are analyzed.

This paper describes an improved iodine pentoxide apparatus and the determination of the liberated iodine by the Beckman spectrophotometer. The revamped iodine pentoxide method was tested on 10 carefully prepared mixtures of carbon monoxide.

Methods and Results

Determination of the Iodine

The determination of the iodine liberated by titration with 0.001 normal sodium thiosulphate was found to be troublesome and inaccurate, especially, when small sample volumes of gas containing low concentrations of carbon monoxide were analyzed. Therefore, it was decided to employ a Beckman spectrophotometer to estimate the iodine in solution. While this investigation was being carried out, a paper by Custer and Natelson appeared (4), in which the spectrophotometer was utilized for the same purpose. The methods for determination of iodine have been reviewed by Custer *et al.*, and Gross *et al.* (4, 8). The colorimetric procedure developed by Gross *et al.* (8) has a sensitivity of 1 to 14 μgm. per 50 ml., while the spectrophotometer method developed by Custer *et al.* (4) has a sensitivity of 0.02 μgm. per ml. The sodium thiosulphate titration is limited to the determination of 7.5 μgm. of iodine per ml. (11) and by the use of organic solvent indicators (5), the sensitivity of the method can be extended to 2 μgm. per ml. (12). Various colorimetric procedures have been developed for the determination of inorganic iodine, but all these methods employ the visible portion of the spectrum where the extinction coefficient for iodine is low. Higher extinction coefficients have been reported for elemental iodine in potassium iodide solutions in the ultraviolet region of the spectrum (3, 16).

A study of the absorption peaks of iodine in toluene, benzene, and potassium iodide in the ultraviolet region has been made (4). It was found that 15% potassium iodide solution was a suitable solvent, that small changes in concentration of potassium iodide solution had little effect on the extinction coefficient, and that a higher absorption peak was evident at 2880 Å than at 3520 Å. Therefore, the determination of iodine in 5% potassium iodide solution, employing the wave length of 2880 Å instead of 3520 Å was used in the present investigation. Preliminary experiments indicated that a plot of iodine concentration versus optical density did not produce a straight line which would go through the origin. This indicated that small amounts of iodine were reacting with free alkali in the solution. In an attempt to overcome the slight alkalinity, the solution was neutralized with acid, but this proved unsatisfactory as small amounts of iodine were liberated. It was decided, finally, to add enough iodine to the potassium iodide solution to take care of

the alkalinity factor and in this way to prevent any iodine, which was to be determined, from being absorbed. To two liters of 5% potassium iodide solution was added 15 ml. of 0.001 normal iodine solution. In the determinations this solution was used as the blank and as the diluent. To prepare a calibration curve, a series of solutions were made, adding iodine solution to the diluent from a microburette to give a concentration range of 0.0 to 4.5 μgm. of iodine per ml. The results are shown in Fig. 1, from which it can be seen that Beer's Law is obeyed over this range.

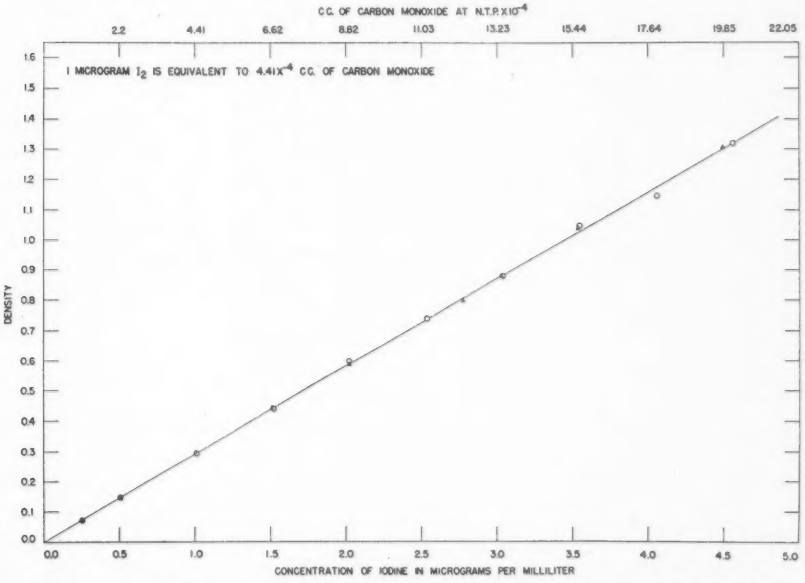

FIG. 1. *Relation between optical density of potassium iodide–iodine solutions and iodine concentration.*

Description of Iodine Pentoxide Apparatus

The function of the purification train of the apparatus is to remove moisture and contaminants such as aldehydes, carbon dioxide, oxides of nitrogen, and hydrocarbons, which might arise from combustion products. Several designs have been described previously for this purpose but have not been effective in reducing the blank determination, without the use of pure nitrogen as a carrier gas. The apparatus shown in Fig. 2 contains a number of improvements which have aided in reducing the blank determination to 1 or 2 p.p.m. The removal of carbon monoxide from the air used in purging the apparatus has, heretofore, not been satisfactory, but with the incorporation of a silver permanganate–zinc oxide reagent developed by Katz *et al.* (9), for the removal of carbon monoxide, this difficulty was alleviated. The removal of hydrocarbons by chromic acid tower and liquid air traps has been described previ-

ously (7, 17). The incorporation of a solenoid valve after the iodine pentoxide reaction tube prevents the absorption of iodine vapor in stopcock grease and gives an air tight system which stops the back diffusion of water vapor into the iodine pentoxide tube. The solenoid valve was constructed from a 12/30 ground glass joint. A bar of iron was sealed into the male part of the joint, and the female part of the joint sealed into the apparatus.

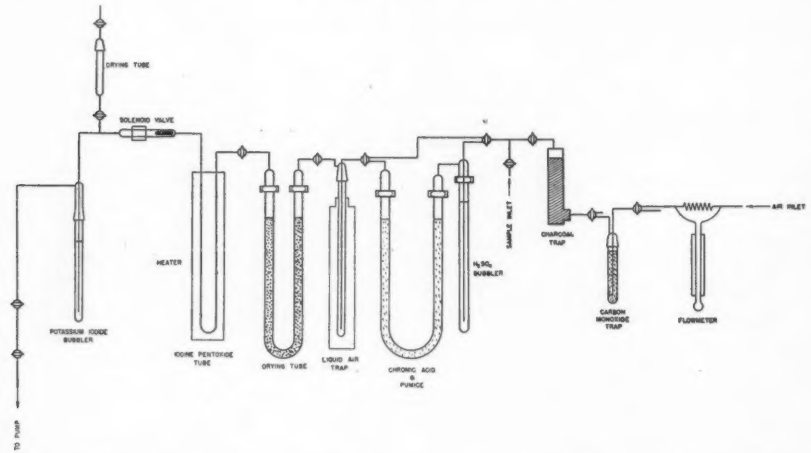

FIG. 2. *Iodine pentoxide apparatus for the analysis of low concentrations of carbon monoxide.*

Operation of the Apparatus

A diagrammatic sketch of the apparatus is shown in Fig. 2. When the apparatus is being swept out with air, either to clean it up before an analysis or to flush the apparatus after an analysis, air is drawn successively through the flowmeter, a carbon monoxide trap filled with silver permanganate–zinc oxide reagent, charcoal trap, liquid air trap, and a drying tube filled with ascarite and magnesium perchlorate. The dry, carbon monoxide free air enters the iodine pentoxide tube maintained at 145°C., and finally passes into the attached potassium iodide bubbler.

For the determination of carbon monoxide in samples containing hydrocarbons, the gas is passed successively through a sulphuric acid bubbler, chromic acid and pumice tower, liquid air trap, drying tube, and finally into the iodine pentoxide tube. The iodine liberated is then absorbed in 5% potassium iodide – iodine solution. To remove the iodine bubbler, the air is allowed to pass through the upright drying tower with solenoid valve closed. The bubbler may then be removed and iodine washed into a flask without allowing moist air to pass back into the iodine pentoxide tube.

To test the purification train, blank carbon monoxide determinations were made on laboratory air. The apparatus was purged with air at a flow rate of

30 cc. per minute, and the iodine pentoxide maintained at 145°C. Some of the results are shown in Table I. After the apparatus was purged for two hours, the blank determination was of the order of one p.p.m. of carbon monoxide. The effect of carbon monoxide concentration on the purging time

TABLE I

IODINE LIBERATED IN TWO HOURS BY PASSAGE OF CARBON MONOXIDE FREE AIR

Sampling time, hr.	Iodine liberated calculated as p.p.m. of CO, by volume
2	0.80
4	0.9
6	1.1

required between analyses was also studied. The results are given in Table II. It is apparent that for concentrations of approximately 0.1% carbon monoxide, it is necessary to purge the system for two and one-half hours to reduce the blank to the original value, while for low concentrations of the order of 0.03% carbon monoxide, one and one-half hours is sufficient purging time.

TABLE II

EFFECT OF CARBON MONOXIDE CONCENTRATION ON PURGING TIME REQUIRED BETWEEN ANALYSES

Purging time, min.	Initial concentration of CO	
	0.138% CO removed in p.p.m. per 30 min. interval	0.0305% CO removed in p.p.m. per 30 min. interval
30	5.5	3.4
60	3.0	2.7
90	2.9	1.3
120	1.6	
150	1.1	

Preparation of Carbon Monoxide and Nitrogen Mixtures

With the above apparatus and the measurement of iodine by the spectrophotometer method, it was felt that low concentrations of carbon monoxide could be measured with greater accuracy than had previously been reported. Thus, it was decided to prepare known mixtures of carbon monoxide and nitrogen in the range of 0.1 to 0.001%.

A sample of 98% carbon monoxide (Mines Safety Appliance Co.) was obtained and analyzed for impurities on the mass spectrograph. The sample contained carbon dioxide, 0.08%; hydrogen, 0.20%; hydrocarbons, 0.50%; nitrogen and oxygen, 1.22%.

A series of dilutions were prepared manometrically. The carbon monoxide was diluted with tank nitrogen which had been previously tested for purity and gave no reaction with iodine pentoxide. Preliminary mixtures containing 10% and 1.0% of carbon monoxide were analyzed on the Blacet–Leighton apparatus by a previously described method (2). The results showed that the gases were not thoroughly mixed. This was probably due to the slow diffusion caused by the geometry of the dilution system employed. A new system was designed as shown in Fig. 3. The incorporation of the heating

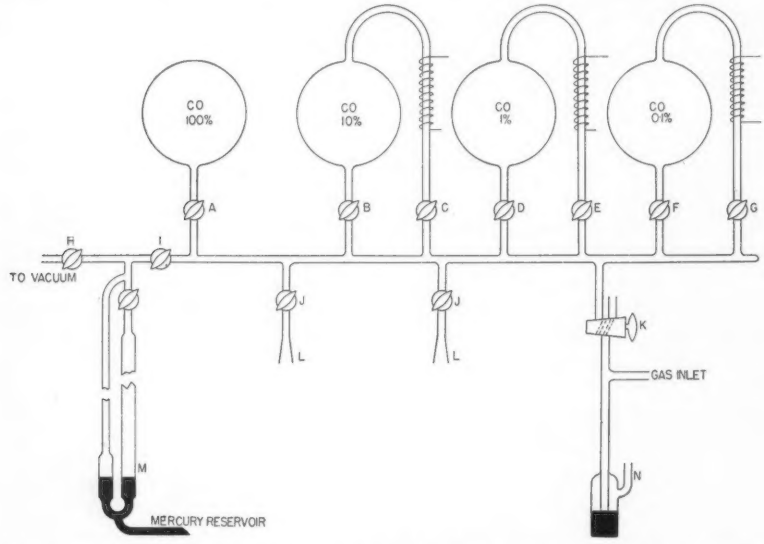

FIG. 3. *Apparatus for the preparation of dilute mixtures of carbon monoxide and nitrogen determinations.*

devices on the side arms leading from the dilution bulbs to the manifold alleviated trouble due to unsatisfactory mixing. The system was evacuated with stopcocks "A" to "I" open. Stopcocks "B" to "H" were closed and 98% carbon monoxide introduced through the mercury cutoff "N" at stopcock "K" and stored in the bulb "A". This stock sample was used in the preparation of all the samples. The rest of the system was then evacuated. Carbon monoxide was introduced to the system from bulb "A" with stopcock "B" and "C" open. Nitrogen was then passed through mercury cutoff "N" to give the required concentration. The chromel wire heaters were then turned on and the whole system allowed to come to equilibrium for 24 hr. Samples were then analyzed by the Blacet–Leighton method (2). Results showed that the gases had been completely mixed. Samples containing 10%, 1%, and 0.1% of carbon monoxide were prepared by the same procedure. The samples for analysis were prepared by attaching a bulb at (L), evacuating the system, and then adding 1% or 0.1% of carbon monoxide and diluting the mixture

with nitrogen. The partial pressures on a constant volume manometer were read by means of a cathetometer to the nearest 0.005 mm. The dilutions were prepared in a constant volume. Thus, only corrections for small temperature changes were necessary.

Results

Analyses were made of 10 samples ranging from 0.000706% to 0.0943% carbon monoxide. The results are shown in Table III. In all but one case the determined values were lower than the calculated values. Percentage

TABLE III

ANALYSIS OF PREPARED CARBON MONOXIDE-NITROGEN MIXTURES

Sample No.	Calculated CO, %	Determined CO, duplicate samples		Average of duplicates	Difference between duplicates	Difference between average and calculated values
		1	2			
1	0.0943	0.0940	0.0938	0.0939	0.0002	−0.0001
2	0.0756	0.0764	0.0755	0.0759	0.0009	+0.0003
3	0.0725*	0.0713	....	....	....	−0.0012
4	0.0475*	0.0474	....	....	....	−0.0001
5	0.0221*	0.0214	....	....	....	−0.0007
6	0.0181	0.0184	0.0174	0.0179	0.0010	−0.0007
7	0.0183*	0.0173	....	....	....	−0.0010
8	0.00542	0.00491	0.00484	0.00488	0.00007	−0.0005
9	0.00175*	0.00166	....	....	....	−0.00009
10	0.000706	0.000661	0.000478	0.000569	0.000183	−0.000137

error for samples containing approximately 0.1% is about 1% while for samples containing 0.002% it is approximately 5%, and for samples containing less than 0.001% it is about 20%. Although the present method will detect carbon monoxide as low as 0.0007% it is not applicable for analytical purposes at concentrations less than 0.001% carbon monoxide.

From the work of Graham (7), it appeared that hydrogen has an effect on the iodine pentoxide, while from other investigations (17), the results seem to be contradictory. Three samples of hydrogen and nitrogen were prepared and passed through the analysis train. The results are shown in Table IV. It

TABLE IV

EFFECT OF HYDROGEN CONCENTRATION ON IODINE PENTOXIDE

Per cent hydrogen	Iodine liberated calculated as % CO
0.50	0.020
0.35	0.014
0.083	0.00173

* *Single determinations.*

appears from these results that hydrogen alone has an appreciable effect on the iodine pentoxide. These results will be commented on in the discussion.

Discussion

Improvements made in the analysis train, together with the adoption of a spectrophotometric determination of iodine has succeeded in reducing the error of determination for carbon monoxide by the iodine pentoxide method. However, in most cases the determined values were lower than the calculated ones. This may be due to the adsorption of iodine on the glass wall after the iodine leaves the iodine pentoxide tube. Another possibility is that the reaction of carbon monoxide with iodine pentoxide may be incomplete under the present conditions. Occasional flaming of the glass tube resulted in the liberation of some iodine from the walls. It is, therefore, suggested that a further improvement in the apparatus could be made by heating the glass tube between the reaction tube and bubbler by means of a nickel–chromel wire heater.

Vandaveer, Gregg, *et al.* (17) state that no reaction with hydrogen and iodine pentoxide occurs in the concentration range of 0.05% to 0.337% hydrogen. It is apparent from the present investigation and that of Graham (7) that hydrogen reacts with iodine pentoxide when the concentration of hydrogen is more than approximately 0.05%. The error due to hydrogen is difficult to overcome, as the conditions such as flow rate of the gas through the apparatus and the temperature of the iodine pentoxide, which are ideal for the complete reaction of the carbon monoxide, are also ideal for the reaction of hydrogen. At the present time, no method is available to remove hydrogen or minimize its effect. Further investigation is needed to obtain a method for carbon monoxide analysis in the presence of high concentrations of hydrogen.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL GASES AND VAPORS

XVII. THE NUCLEAR IGNITION OF *n*-PENTANE IN THE C.F.R. ENGINE AND THE EFFECT ON PERFORMANCE[1]

By R. O. King,[2] E. J. Durand,[3] and A. B. Allan[4]

Abstract

Temperature and carburetion conditions were such that the pentane could persist during compression in part as liquid drops. Finely divided carbon in the concentration necessary for nuclear ignition could then be obtained by thermal cracking at temperatures and pressures attained during the compression stroke. The concentration so obtained was augmented by the carbon formed on burning rich mixtures surrounding droplets of pentane and on the impingement of the flame of such mixtures on the cool surfaces of the combustion chamber. In these circumstances, the engine ran without spark ignition, a standard intensity of knocking combustion being maintained by varying the compression ratio in accordance with change in mixture strength. Indicated thermal efficiencies for mixture strengths varying from 30% weak to 40% rich were, on the average, 83% of ideal values. A maximum value of 53% was obtained for indicated thermal efficiency when using a mixture 60% weak at a compression ratio of 11.5:1, the I.M.E.P. being 98 p.s.i. This surpasses the value of 51.6% accompanied by an I.M.E.P. of 66 p.s.i. obtained with a Diesel engine at 15:1 C.R. and commonly regarded as a record. The experiments provide confirmatory evidence for the nuclear theory of ignition advanced in Part IV and indicate that autoignition by compression, in general, is a nuclear effect arising from a decomposition reaction.

Introduction

The finely divided carbon giving rise to detonation when benzene was used as an engine fuel was formed by the burning of rich mixtures after flame had been initiated by a spark, Part XVI (2). Thus detonation in a particular combustion period could be attributed to the igniting effect of carbon nuclei which had been formed during prior periods, an essential condition being that the carbon is of the powdery form, capable of being dispersed in the combustible mixture by the entering turbulence. The engine would, therefore, not run without spark ignition because an igniting concentration of finely divided carbon was not obtainable in the time available by decomposition (cracking) of the benzene at the temperatures and pressures attained during the compression stroke.

Normal paraffins are principal constituents of "cracking stock", whereas cyclic compounds such as benzene are final products and, in the cracking process, the paraffins yield some proportion of carbon at temperatures and pressures lower than those attained during the compression stroke of an engine.

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The experiments described in this Part were made in the conditions most favorable for the formation of finely divided carbon during the compression stroke. Pentane was used as the fuel and although it is more resistant to cracking than higher members of the paraffin series, compression ignition was obtained at a piston position such that the engine would run without spark ignition at compression ratios varying from 6.8 to 12: 1. Performance in terms of indicated thermal efficiency and mean effective pressure was equal to or superior to that obtained at comparable compression ratios with spark ignition or Diesel operation.

Experimental Arrangements

The arrangements were, in general, as described for the experiments with benzene (2). The C.F.R. engine was standard except that the shrouded inlet valve was replaced by one of the common tulip type and the limit of compression ratio measurement was extended to 13: 1.

The normal pentane was the technical grade as supplied by Phillips Petroleum Co. A lower calorific value of 19,500 B.T.U. per lb. was used for calculations of thermal efficiency as based on the usual dynamometer measurements of power and friction loss.

The jacket cooling water entered at 85°F. and flow was adjusted automatically to limit the temperature rise to 5°F.

The standard mixture heating chamber was removed and the carburetor bolted directly to the engine head. The diffuser was removed from the carburetor to allow the pentane to enter the venturi throat as a completely liquid jet and thence pass into the engine mainly as liquid drops.

The air metering equipment was set up outside the laboratory building in an open shed and the experiments made in midwinter. The air metering temperature remained nearly constant, at 44°F., during the time required for the experiment; the relative humidity was 56%. The temperature of the air rose to 63°F. while it passed to the carburetor inlet through 20 ft. of bare 3 in. steel pipe in the warm laboratory. The relative humidity was then 28% and ice did not form in the carburetor although vaporization of the pentane reduced the temperature by from 47° to 23°F., depending on mixture strength.

The temperature and entry conditions ensured that the pentane remained in part throughout compression as liquid drops. The drops while slowly evaporating would be surrounded by nearly pure vapor. The physical state most favorable for the formation of carbon by the cracking process was thus provided. The relatively low engine speed of 400 r.p.m. used for the experiments provided the "delay period" necessary for the finely divided carbon to attain the concentration required for ignition of pentane vapor – air mixture.

Experimental Results

The C.F.R. engine had been dismantled and cleaned a few days before the experiments were undertaken. The combustion space was, however,

given a final cleaning with special scrapers and brushes. The engine was then run for three hours in order to stabilize temperatures. The inlet air temperature was 62.6°F., jacket coolant 85° to 90°F., speed 400 r.p.m., and compression ratio 5.5:1. The mixture strength and spark advance were adjusted for maximum power.

On completion of the stabilizing run, spark advance was set at the more retarded value of 10° and compression ratio raised until "standard" knock intensity, as indicated by a midscale reading of the knockmeter, was obtained. The intensity adopted as standard was somewhat greater than generally used for routine fuel testing but was well below that of knock limited power. The knockmeter had been adjusted to give a midscale reading for the adopted standard intensity. The engine ran fairly steadily without spark ignition at 7.7:1 C.R. while maintaining standard knock intensity.

It was observed that running became quite steady, with the appearance of continuing indefinitely, on increasing compression ratio to give a knock intensity greater than standard but still less than that at which power reaches a maximum. The intensity adopted as standard had, however, been used for so many earlier experiments that it was decided to continue with it.

Running without spark ignition continued to be not entirely steady over an intermediate weak mixture range but became quite steady for a mixture 53% weak, compression ratio being then 11.3:1. Steady running without spark ignition continued as mixture strength was reduced to 60% weak and compression ratio raised to 11.5:1. That is, especially steady running without spark ignition was obtained at Diesel engine compression ratios.

The experiment was continued but on the rich mixture side, beginning with a mixture 17% rich for which U.C.R. was approximately 7:1. Mixture strength was increased by steps until at 74% rich, U.C.R. attained a value of 12.4:1, approximately the maximum measurable. The engine ran somewhat unsteadily and with variable knock intensity, without spark ignition. Nevertheless, after being stopped it could be restarted without spark ignition, indicating that the unsteady running was due to the amount of residual carbon being variable, as would be expected.

The experiment was completed by observations at nearly correct mixture strength, namely, 5.6% weak, 2.5%, and 5%, rich U.C.R. values being 7.7, 7.2, and 6.9:1, respectively. The engine ran smoothly with standard knock intensity nearly constant and without benefit of spark ignition. It will be noted that the steady running on mixtures nearly correct was obtained when the combustion chamber would be expected to contain residual carbon due to previous running on over-rich mixtures. The combustion chamber surface was then viewed through the spark plug hole and, so far as it could be inspected with the aid of interior lighting, was seen to be free of the adherent type of hard carbon and nearly so of the lamp black type.

The experimental results for engine performance are given by the graphs of Fig. 1. Values of mean effective pressure in pounds per square inch are obtainable by multiplying values of horsepower by the factor 53.1. Significant performance data are given in Table I and related values of ideal efficiencies for

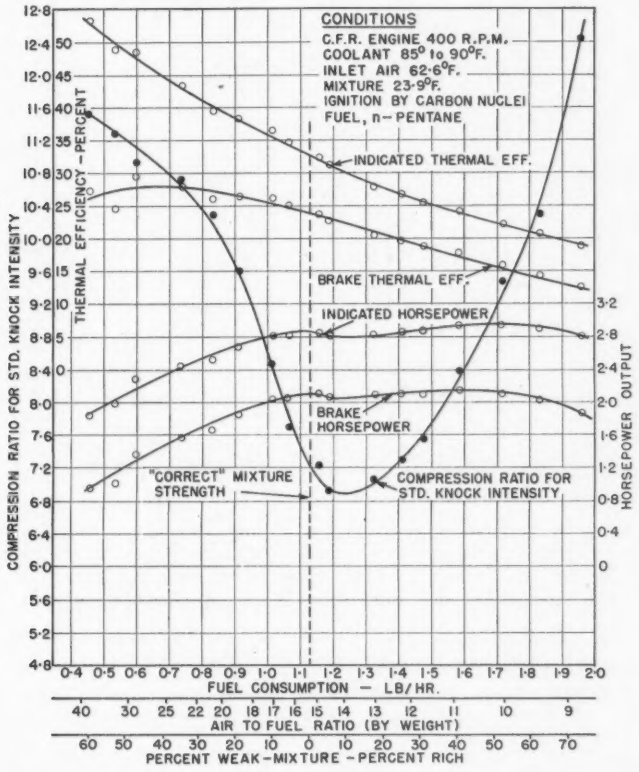

FIG. 1. *Graphical presentation of data for power and thermal efficiency, pentane–air mixtures 60% weak to 74% rich.*

mixture strengths of from 30% weak to 40% rich are given in the last column of the table. The ideal efficiencies are those calculated by Prof. C. Fayette Taylor, Massachusetts Institute of Technology, from the most recent thermodynamic data and are given, by permission, from unpublished work.

It will be noted that a high performance was obtained in terms of I.M.E.P. It was no doubt due mainly to the high volumetric efficiency obtained in the experimental conditions. The experimental values of indicated thermal efficiency taken over the range of mixture strengths mentioned average 83% of the ideal values given by Taylor.

The ideal efficiency for a benzene–air mixture 50% weak is given by Pye as 50% (4, p. 181) at a compression ratio of 10: 1. The value obtained for a 50% weak pentane–air mixture was 48% but at a compression ratio of 11.2: 1. The observed value of indicated thermal efficiency for a mixture 60% weak was 53.6% at a compression ratio of 11.5: 1, I.M.E.P. being 98 p.s.i. A

TABLE I

PERFORMANCE DATA FROM FIG. 1

Pentane–air mixture	Usable C.R.	I.M.E.P., lb.	I.T.E., %	Ideal efficiency, Taylor, %
60% weak	11.5: 1	98	53	
30% weak	10.4: 1	133	42	49
Correct	7.5: 1	150	33	42
10% rich	6.9: 1	149	30	37
40% rich	8.3: 1	157	24	28
75% rich	12.4: 1	149	18	

value of 51.6% obtained by Ricardo is quoted by Pye (4, p. 216) as being the highest on record. It was obtained for a direct injection (Diesel) sleeve valve engine at 1300 r.p.m. and I.M.E.P. was 78 p.s.i. as compared with the value of 98 p.s.i. for the carburetor engine.

The comparisons of observed indicated thermal efficiencies with ideal values are given mainly to show that the ability to run the engine on nuclear instead of spark ignition was not accompanied by a sacrifice of performance. The comparisons can be approximate only because the ideal efficiencies quoted were calculated on the basis of an initial temperature of compression of 100°C. The initial compression temperature of the experiments with pentane was lower to an unknown and variable extent. Moreover, the dynamometer method of measuring indicated thermal efficiencies is not regarded as being of a high order of accuracy in the extreme conditions of temperature, and combustion pressures of the experiments.

Discussion

When a carburetor engine runs with the spark ignition switched off, it is generally "hot" and ignition is commonly supposed to be by some overheated surface in the combustion chamber. When, however, a cold engine runs without spark ignition, with unheated air supply and pentane as the fuel, while at the same time developing the power possible at the usable compression ratio, ignition must occur *in* the fuel–air mixture and arise in some way from the heat of compression. In these circumstances, a carburetor engine becomes a compression ignition engine and the mechanism of ignition must be the same as that in a Diesel engine or in a laboratory compression ignition apparatus making a single compression stroke.

The mechanism of ignition will be discussed for the purpose of determining the extent to which experimental results for compression ignition accord with

the nuclear theory of ignition advanced in Part IV (1). The theory is based on the assumption that heating of the fuel–air mixture solely by compression leads to ignition if decomposition of the fuel provides a sufficient concentration of finely divided material. The material would be carbon if that substance is contained in the fuel molecule. The theory was applied to explain the auto-ignition obtained with spark ignition at the high temperature and pressure of the end gas. It is necessary for present purposes to consider how carbon nuclei of ignition can be obtained at the lower temperatures and pressures attained at or near the end of the compression stroke.

Sources of the Finely Divided Carbon Required for Nuclear Ignition in Engines

The carbon is obtainable from one or a combination of four sources, namely (*a*) pyrolysis of the lubricating oil, (*b*) the impingement of the flame of rich mixtures on cool surfaces, (*c*) the burning of rich mixtures surrounding evaporating liquid drops, (*d*) the thermal cracking of completely vaporized fuel, or (*e*) the cracking of the nearly pure vapor and rich mixture surrounding liquid drops.

It was shown by experiments with hydrogen, Part V (3), that, starting with a clean combustion chamber, several hours of engine running time elapsed before the finely divided carbon derived from pyrolysis of the lubricating oil accumulated to the extent required to ignite the hydrogen–air mixture. It is assumed therefore that source (*a*) need not be taken into account when a relatively large supply of carbon is obtainable from fuels containing the substance in the molecule.

Carbon is obtainable from sources (*b*) and (*c*) *after* flame has been initiated by spark ignition. Carbon obtained accordingly may in part remain in the combustion chamber and, on being dispersed by the turbulence of the incoming charge, provide the nuclear concentration required for ignition. The igniting effect may be described as secondary. It provided the ignition required for knocking combustion when benzene was used in cool engine conditions, Part XVI (2), but the engine would not run without benefit of spark ignition.

The finely divided carbon required for primary nuclear ignition at every firing stroke must be obtained from source (*d*) when the fuel in the mixture with air is vaporized completely or from sources (*d*) and (*e*) if vaporization is partial. Higher temperatures and pressures would be required to obtain the necessary carbon from source (*d*) than from (*e*). The nuclear concentration from either or both sources, when adequate to start a flame at or near the end of one compression stroke, would be augmented for subsequent strokes by carbon from sources (*b*) and (*c*) if rich mixtures were used or if mixtures were weak overall but not homogeneous. The concentration formed per compression stroke from sources (*d*) and (*e*) would be expected to decrease with engine speed and with increase in the resistance of the fuel to cracking. It would be expected to increase with compression ratio and with increase of charge pressure which determines the quantity of "cracking stock" admitted per stroke at any particular mixture strength.

Manifestations of Nuclear Ignition in the Carburetor Engine

It is generally assumed that in the usual circumstances of engine operation, evaporation of the fuel is complete by the end of compression. It is safer to assume that it is complete in the end gas. The concentration of finely divided carbon required for primary nuclear ignition and consequent detonation must then be obtained from source (*d*), that is, by vapor phase cracking, assuming that the fuel had been vaporized before cracking began. The time required for the accumulation of an igniting concentration is then regarded as a delay period of rising temperature and pressure. It may therefore extend over a time interval beginning before spark ignition and ending with nuclear ignition of the end gas, late in the combustion period. Detonation giving knocking combustion *after* spark ignition is thus obtained and, as is well known, temperature and pressure, that is, compression ratio, must be raised as speed is increased and the delay period shortened in order to maintain a standard knock intensity. Similarly, when the temperature and pressure are increased by increasing compression ratio at constant speed, the formation of carbon nuclei begins earlier and proceeds with increased rapidity. The result is that the delay period moves toward lower compression pressures, nuclear ignition occurs in a larger volume of end gas, and knock intensity increases.

The reason why the C.F.R. engine ran without spark ignition in the conditions of the experiments described in this part is therefore that the delay period began relatively early in the compression period. This was possible because the pentane was admitted mainly as liquid drops and carbon was obtainable from source (*e*), relatively low temperatures and pressures being required for cracking. The engine speed in addition was relatively low, 400 r.p.m., and, the delay period being lengthened accordingly, the igniting concentration of carbon nuclei was obtained at a piston position such that spark ignition was no longer required. Nuclear ignition timing in the circumstances was adjustable, within limits, by raising or lowering the compression ratio. That the position corresponding to the compression ratio for the standard knock intensity was suitable for a satisfactory engine performance in terms of thermal efficiency and power is apparent from the data of Table I.

The whole combustible charge becomes the end gas when nuclear replaces spark ignition. The knocking combustion obtained cannot be true detonation, defined as nearly simultaneous ignition throughout the mass of the charge. True detonation, with probably disastrous consequences to the engine, could occur solely if closely packed nuclear centers were distributed uniformly in the combustible mixture. The conditions required could be approached if temperatures and pressures were high enough for vapor phase cracking and if nuclear concentration were increased by supercharging.

It was mentioned earlier that the knocking combustion obtained when using benzene could be attributed to carbon obtained from sources (*b*) and (*c*), that is, after flame initiated by a spark had passed through the combustible mixture. When using pentane, carbon was obtainable from the same sources

as well as from sources (*d*) and (*e*), and observed characteristics of the consequent knocking combustion were as would be expected accordingly. The experiments with pentane were begun with a mixture 17% weak and a clean combustion chamber. There was then no accumulation of carbon and the engine ran somewhat unsteadily without spark ignition and with compression ratio adjusted for standard knock intensity. Quite steady running was, however, obtained on increasing the compression ratio and the consequent knock intensity or on using weaker mixtures thus making it possible to increase compression ratio while maintaining standard knock intensity. It would be expected that a change to rich mixtures would increase residual carbon from sources (*b*) and (*c*) and augment the concentration derived from sources (*d*) and (*e*). As shown by the graph for U.C.R., Fig. 1, compression ratio for standard knock intensity reached the limit of measurement when mixture strength was increased from 10% to 70% rich. The somewhat unsteady running obtained when rich mixtures were used without spark ignition is attributed to the difficulty of maintaining a suitable quantity of residual carbon in the physical state required for dispersion by turbulence, throughout the mixture. However, the engine could be started on rich mixtures without spark ignition. Also on changing quickly from rich mixtures to the weaker ones near the correct value, running without spark ignition was quite steady whereas before rich mixtures had been used it was somewhat unsteady, unless the compression ratio were increased to make knock intensity greater than standard.

Conclusion

The "autoignition" obtained after a delay period when gaseous combustible mixtures of fuel vapors and air are compressed in a single stroke apparatus is regarded as a manifestation of nuclear ignition. Similarly the combustion delay period in the direct injection (Diesel) engine is regarded as the time required for the cracking of part of the fuel to yield the concentration of finely divided carbon required for ignition of a vaporized part. It is reasonably possible to go even farther and regard the detonation in tubes, obtained after a short run of flame, as being due to nuclear ignition.

The value of 53% for indicated thermal efficiency was obtained when the mixture was 60% weak and the difference between brake and lost horsepower relatively small. Values measured by the dynamometer method must, in the circumstances, be approximate only. The real interest of the experiments lies in the demonstration of the extent to which spark ignition can be replaced by nuclear ignition in a carburetor engine and the consequent contribution to our knowledge of the mechanism of combustion.

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